OUTLINES OF PHYSICAL CHEMISTRY

FARRINGTON DANIELS

Chap 6 - 2,3,5,6,8,9,10,11,13,15,16,18,19,20,23

7 1,2,4,5

8 1,2,6,7,9,11,12,13,14,26,[illegible]32,34,36,38 (in 4 → 40-4

9 1,20,26

Def. 12,14,16,23

1 - 11 (in 3)

1-3, 5,7,8,18,19,22-29,37 Derive 30

31,6,8,9, 23-27, 29-31, 37, 38, 40 (41)

Derive 11,13,15,17,20

M. Katz
219 Bay 32nd St
B'klyn 14 N.Y.
CO 6-4919

Augis
Sept 2

134

375

Samuel - Gus Feld
Earley
James
James Earley

STUDENT'S NAME .....
SCHOOL .....
CLASS & NO. .....
THIS BOOK SOLD BY
E-K BOOK EXCHANGE
14 WASHINGTON PLACE
N. Y. C. 3 (next door to luncheonette)
WE'LL BUY IT BACK FROM YOU
HIGHEST PRICES PAID FOR USED TEXTBOOKS

OUTLINES OF
PHYSICAL CHEMISTRY

Digitized by the Internet Archive
in 2026

https://archive.org/details/bwb_C0-CZT-184

OUTLINES OF

PHYSICAL CHEMISTRY

FARRINGTON DANIELS

Professor of Chemistry, University of Wisconsin

1948 *Third Printing Corrected*

JOHN WILEY & SONS, INC. NEW YORK

CHAPMAN & HALL, LIMITED LONDON

Copyright, 1913, 1918, 1922, 1927
as "Outlines of Theoretical Chemistry"
by FREDERICK H. GETMAN

1913 Copyright Renewed 1940
1918 Copyright Renewed 1945

Copyright, 1931, 1937
as "Outlines of Theoretical Chemistry"
by FREDERICK H. GETMAN and FARRINGTON DANIELS

Copyright, 1943
as "Outlines of Physical Chemistry"
by ELLEN H. GETMAN and FARRINGTON DANIELS

Copyright, 1948
by JOHN WILEY & SONS, INC.

All Rights Reserved

This book or any part thereof must not be reproduced in any form without the written permission of the publisher.

THIRD PRINTING, CORRECTED, JULY, 1949

PRINTED IN THE UNITED STATES OF AMERICA

PREFACE

"Outlines of Physical Chemistry" seeks to provide material for a first course in physical chemistry. The author has endeavored to make it clear and interesting, with emphasis on practical examples, but without sacrificing the fundamental mathematical developments on which it is based. In this effort he owes much to contact with many student classes, to the advice of his several colleagues through the years at the University of Wisconsin, and to a wealth of helpful suggestions which have come from teachers all over the world. He greatly appreciates these suggestions and welcomes continuing comments designed to improve the book in possible future editions.

"Outlines of Theoretical Chemistry," as it was then named, was first written in 1913 by Dr. Frederick H. Getman, who carried it through 1927 in four revisions. Dr. Getman did excellent work in bringing together for elementary students the early developments of physical chemistry. We are grateful for his pioneer work.

In 1930 the present author accepted the responsibility for writing the book and his four succeeding revisions have been so extensive that nothing remains of Dr. Getman's earlier editions. In each revision the author has raised the level of presentation to keep pace with the improved preparation with which students are starting the study of physical chemistry. He has endeavored also to translate for student use the advances in physical chemistry which are coming so rapidly and are finding such important applications in all branches of chemistry, in engineering, in biology, and in many other sciences.

The present work is regarded as the first edition of a new book, in which the author has attempted to meet his responsibilities for better presentation of physical chemistry by adding recent developments in the field, clarifying descriptions, eliminating some of the more elementary material, rearranging chapters, and transferring some of the more specialized parts to the appendix. He has tried to bring out fundamental principles and to give glimpses of the frontiers of physical chemistry.

Many new problems have been substituted for old ones, thought-provoking problems being stressed rather than the formula-illustrating type. Different types of problems are offered in each chapter to meet the needs of students coming to physical chemistry from different edu-

cational backgrounds and with different purposes. Again the more thorough student is referred to the appendix for the derivation of certain formulas which the more hurried student will prefer to take for granted.

The author is particularly indebted to Professor Thomas F. Young, of the University of Chicago, for many penetrating criticisms and helpful suggestions. He wishes to thank Dr. Darrell W. Osborne, of the Argonne National Laboratory, and Professor George W. Murphy, of the University of Wisconsin, for criticisms of parts of the manuscript, and Professor Paul Bender and other members of the physical chemistry staff at the University of Wisconsin for examination of parts of the book. He is indebted to Mr. D. B. Hu, Mr. G. O. Michaels, and Mr. W. A. Rowe and others for help in checking some of the calculations and problems.

FARRINGTON DANIELS

Madison, Wisconsin
September 1948

CONTENTS

1	Introduction	1
2	The Gaseous State	5
3	Atomic and Molecular Forces	33
4	The Crystalline State	42
5	Physical Properties and Molecular Structure	67
6	Heat, Work, and Heat Capacity	99
7	Thermochemistry	124
8	Thermodynamics	142
9	The Liquid State	166
10	Solutions	194
11	Solution of Nonvolatile Solutes	227
12	Chemical Equilibria	254
13	Phase Diagrams	304
14	Chemical Kinetics	342
15	Electric Conductance	395
16	Electromotive Force	431
17	Ionic Equilibria	483
18	Colloids	523
19	Quantum Theory	565
20	Photochemistry	593
21	Atomic and Nuclear Structure	617
	Appendix	671
	Author Index	701
	Subject Index	706

Table of Important Constants

The following approximate values will be used for problems. Most of them are sufficiently important to memorize during the course of the work.

Acceleration of gravity	**980.7**	cm sec^{-2}
Molar volume (0°, 1 atm)	**22.41**	liters $mole^{-1}$
Ice point (0°)	**273.1°**	K
One calorie (defined)	**4.184**	joules
R	**8.314**	joules deg^{-1} $mole^{-1}$
R (calorie)	**1.987**	calories deg^{-1} $mole^{-1}$
R (liter-atmosphere)	**0.08205**	liter-atm deg^{-1} $mole^{-1}$
Faraday	**96,500**	coulombs gm $equiv^{-1}$
	23,060	calories $volt^{-1}$ gm $equiv^{-1}$
Avogadro number	$\mathbf{6.02 \times 10^{23}}$	$mole^{-1}$
Planck's constant	$\mathbf{6.62 \times 10^{-27}}$	erg sec
Velocity of light	$\mathbf{3 \times 10^{10}}$	cm sec^{-1}
Conversion $\log_{10}$ to $\log_e$	**2.303**	

These and other constants are given with the highest precision now warranted, on page 699.

CHAPTER I

INTRODUCTION

Survey of Physical Chemistry. The purpose of the study of physical chemistry is to understand and apply the laws of chemistry and physics.

Physical chemistry emerged as a separate branch of science in the latter part of the last century. It has continually broadened its scope with new discoveries and has become more exact with improvements in experimental measurements and with greater use of mathematics. The boundaries of physical chemistry are not sharp; they overlap physics on the one side and all branches of chemistry on the other. Physical chemistry draws its facts from all these fields of knowledge and correlates them by means of word descriptions, graphical representations, and mathematical formulas. Of these the mathematical formulas are the most powerful. Thus, there has been a decided trend toward the use of more mathematics in chemistry.

In the study of physical chemistry as presented here, the physical properties of gases and crystals are described first. The equations of state and the kinetic theory have been a great help in studying the behavior of gases; and the application of X-ray measurements has given a clear picture of the nature of solids. Valence and the types of forces which hold atoms and molecules together are studied immediately after the discussion of gases. Many physical properties may be predicted from the known structure of the molecules; and, conversely, the arrangement of atoms within the molecule can often be determined from the measurements of physical chemistry. Because of the prevalence among organic compounds of rigid bonds rather than the more mobile electrical attractions, the discussion of molecular structure is confined chiefly to the field of organic chemistry.

Practically all changes studied in chemistry and physics involve a change in energy. Since energy can be measured quantitatively and easily, it constitutes an excellent means for describing and predicting the phenomena of physical chemistry. Part of the energy can be made to do useful work, and part of it cannot. The useful available work is of fundamental importance in physical chemistry.

Quantitative energy relations are introduced as soon as a background of facts has been established, and they run through much of the ma-

terial of the remainder of the book. The familiar concepts of work, heat, and heat capacity are followed by a presentation of thermochemistry and then by a presentation of the more abstract concepts of thermodynamics which are concerned with the relations among work, heat, and chemical reactions. Further applications in chemical thermodynamics are presented later, particularly in the chapter on chemical equilibria.

The theory and properties of liquids are taken up next, after a background of thermodynamics has been established.

A notable part of physical chemistry is devoted to the properties of solutions. Ideal solutions, which follow simple laws, are discussed first and then solutions of nonvolatile materials. Such properties as freezing-point depression, boiling-point elevations, and osmotic pressure are related directly to the lowering of vapor pressure in solutions. Nonideal solutions and particularly ionic solutions require special treatment.

The questions of how far a chemical reaction will go and what percentage of the initial material will be converted into final products under various conditions are studied quantitatively with the help of equilibrium constants.

The presentation of relations between different phases which are in equilibrium is illustrated with typical diagrams. The phase rule of Willard Gibbs plays an important part in their interpretation.

Although the problem of how far a reaction will go has been largely solved through thermodynamics, little is known concerning the speed with which it will go. This subject is considered in chemical kinetics. The various expressions for reaction rates and the mechanisms proposed to account for the reactions are discussed.

Much of the latter part of the book is devoted to relations between electricity and chemistry. It deals first with the electrical conductivity of solutions and with changes occurring at the electrodes when an electric current is passed through the cell. Then the electromotive force of cells is studied both from a theoretical and a practical standpoint. Finally, the chemical behavior of electrolytes is considered.

When a material is subdivided into exceedingly small units (but larger than molecules) and spread through a liquid or other medium, the surface area is increased enormously, and the electric charges and the attraction for the solvent then become dominating factors and introduce important new phenomena. These relations are discussed under colloid chemistry.

A brief introduction to the quantum theory and spectroscopy is necessary not only for the study of photochemistry but also for the study of many other branches of modern chemistry.

Molecules usually must be activated by the addition of energy before they can react chemically. One of the simplest ways in which they become activated is through the absorption of light. Therefore, the study of photochemistry is important not only in itself but also because of the information which it gives about the mechanism of chemical reactions.

Rapid developments have occurred in our knowledge of the structure of the atom, particularly with respect to the nucleus. It has been shown that the atoms are composed of very dense positively charged nuclei surrounded by small negative electrons. The nuclei in turn are composed of smaller units; protons, which are the nuclei of hydrogen atoms and neutrons, which have nearly the same weight as the hydrogen nuclei but no charge.

Extraordinary advances have been made in breaking down these nuclei with neutrons and by bombardment with charged particles at very high voltages. These advances have led to the production of many new isotopes, to a broad extension of radioactivity, and to the production of nuclear energy on a large scale.

Fundamental Units. The phenomena of chemistry and physics are concerned with matter at rest or in motion, with electricity, and with radiation. Marked progress has been made in understanding these phenomena by visualizing the primary units involved—the atom and the molecule of matter, the electron of electricity, and the photon of radiation. It has been found experimentally that there are 6.02×10^{23} molecules in a gram molecule or mole, and this number has become an important constant of physical chemistry known as the Avogadro constant. This constant enables one to predict from the behavior of individual atoms, electrons, and quanta what will be the behavior of ordinary material. For example, the quantity of electricity called the Faraday, which will electrolyze a gram equivalent of ions, is obtained by multiplying the charge on the electron by the Avogadro constant. This constant, 6.02×10^{23}, is so large that it is difficult to visualize. Very few practical operations can be carried out in chemistry which involve less than a millionth of a mole, but even a millionth of a mole contains almost a billion billion molecules.

As far as possible in scientific work, measurements are expressed in terms of centimeters, grams, and seconds, and their derived units, that is, in the cgs system.

Ergs, the fundamental units of energy, are based on the centimeter, the gram, and the second. The centimeter is defined in terms of a standard meter bar and the gram in terms of a standard kilogram weight; both bar and weight are very exact standards kept in government lab-

oratories for reference. The second is defined by means of astronomical observations.

Scientific Method. Chemistry and all other sciences are based on experimentally established facts. When a number of facts have been collected and classified, we may draw inferences as to the probable behavior of systems under conditions which have not been investigated. When a number of phenomena have been observed and studied with exact measurements, we can often develop a *law* which will predict the behavior of similar systems under different conditions. The law is not necessarily an expression of infallible truth but is rather a condensed statement of facts which have been discovered by experiment. It enables us to obtain facts which are needed without continued recourse to experiment.

Natural laws may be discovered either by the correlation of experimentally determined facts, as we have just shown, or by means of a speculation as to the probable cause of the phenomenon in question. Such a speculation regarding the cause of a phenomenon is called an *hypothesis*. After an hypothesis has been subjected to the test of experiment and has been shown to apply to a large number of phenomena it is termed a *theory*.

Usually science progresses by inductive reasoning from a few facts, follows with deductive reasoning based on the hypotheses, and, finally, tests by experimental measurements designed to prove or disprove the theoretical deduction.

Many hypotheses are destined to be discarded when new facts and more precise data are obtained, but they fulfil a very necessary function in the development of science. A successful hypothesis is not necessarily a permanent hypothesis, but it is one which stimulates additional research, opens up new fields, or explains and coordinates previously unrelated facts. The scientist needs imagination in creating new hypotheses, but he needs also ingenuity and skill in devising experiments to test them and critical judgment in evaluating the results.

The scientific method has been so effective and has made possible such an increase in commodities, transportation, communication, medicine, warfare, agriculture, industry, and most of the physical aspects of life that the scientists have come to have an importance they little envisioned in their humble search for facts and theories. With the availability of atomic energy they have come to realize that their findings have consequences which need to be as intelligently controlled out of the laboratory as within and on a major and world-wide scale. Their concerted efforts to educate public and governments in the need of such controls represents a new step in human responsibility at a most critical time.

CHAPTER II

THE GASEOUS STATE

The Behavior of Ideal Gases. The gaseous state is characterized by the fact that the molecules are so far apart that they exhibit only slight attraction for each other, thus permitting the material to expand and fill completely a containing vessel of any size or shape. As a first approximation, the physical behavior of a gas is not affected by the chemical nature of its molecules, and, thus, all gases respond in nearly the same way to the variables, pressure, volume, and temperature.

In an ideal gas there is no interaction whatever between the molecules, and the chemical energy of the gaseous material remains unchanged if the gas is expanded into a larger volume.

The relation among the three variables, pressure, volume, and temperature, in an ideal gas is given by the simple gas law:

$$pv = nRT \tag{1}$$

where p is the pressure, v is the volume, n is the number of moles of gas, T is the absolute temperature,* and R is a constant known as the gas constant and defined in the following section.

In the special case where 1 mole of gas is taken, $n = 1$ and

$$pV = RT \tag{2}$$

the capital V signifying the volume of 1 mole of the gas.

This gas law is a mathematical formula which expresses the relations among pressure, volume, and temperature which have been found by experiment. It is shown in a later section, however, that, when the experimental measurements are made with high accuracy or at high pressures, deviations from this simple gas law are found.

The first experiments on which this law is based were performed by Robert Boyle in 1662 who found that at constant temperatures the volume of a gas decreases when pressure is applied and that it is inversely proportional to the applied pressure, a fact which can be expressed mathematically by the formula:

$$v = \frac{k_1}{p} \quad \text{(temperature constant)}$$

* T is used for absolute temperature; t for temperature on the centigrade scale.

where k_1 is a constant. This important relation between the pressure and volume of a gas is shown graphically in **Fig. 1.** The curve plotted here is a special case of a hyperbola, sometimes called a reciprocal curve.

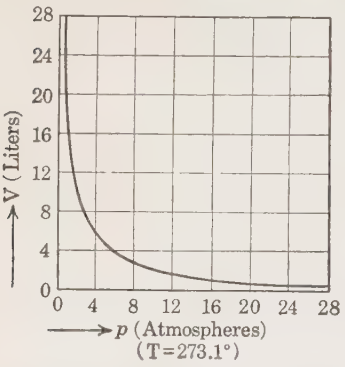


FIG. 1. Volume of 1 mole of an ideal gas plotted against pressure at constant temperature.

In 1802 Gay-Lussac reported his discovery of the relation between the volume of a gas and its temperature. In unpublished earlier work, Charles had found that certain gases expand to the same extent when the temperature is increased. Interpreted in modern terms this law states that at constant pressure the volume of a gas is directly proportional to its absolute temperature, as given by the formula,

$$v = k_2 T \quad \text{(pressure constant)}$$

and by **Fig. 2,** in which the direct proportionality between the two variables necessarily gives a straight line. The dotted line indicates that many gases will liquefy at the lower temperatures and that the relationship applies only to material which remains as an ideal gas.

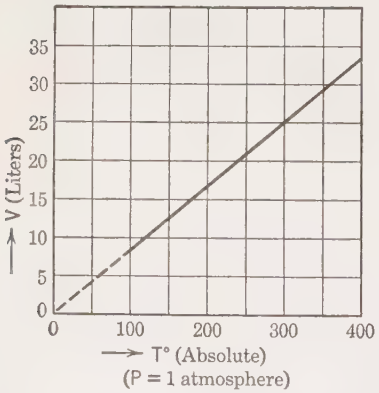


FIG. 2. Volume of 1 mole of an ideal gas plotted against absolute temperature at constant pressure.

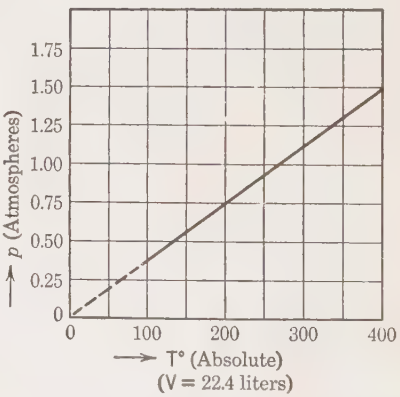


FIG. 3. Pressure of 1 mole of an ideal gas plotted against absolute temperature at constant volume.

If the volume is kept constant, it follows that the pressure of the gas is directly proportional to its absolute temperature as shown by the formula,

$$p = k_3 T \quad \text{(volume constant)}$$

and by the straight line in **Fig. 3.**

The combination of Boyle's law and the law of Gay-Lussac and Charles * leads, as shown in the appendix on page 671, to the expression

$$pv = \text{constant} \times T$$

which is equivalent to the general expression for the behavior of an ideal gas given in equation 1.

The Gas Constant. With reference to equation 2,

$$pV = RT$$

it has been found by many careful experiments, in which corrections are made for slight interactions between the molecules, that 1 mole (that is, 1 molecular weight in grams) of an ideal gas occupies 22.414 liters at 0° C or 273.16° K.†

Then,

$$R = \frac{pV}{T} = \frac{1 \text{ atm} \times 22.414 \text{ liters}}{273.16°}$$

$$= 0.08205 \text{ liter-atm degree}^{-1} \text{ mole}^{-1} \ddagger \qquad (3)$$

It should be noted that the molar gas constant has the dimensions of energy per mole divided by temperature. The term pV is a form of energy because it involves a force acting through a distance.

The pressure may be changed to dynes per square centimeter by multiplying the barometer height, 76 cm of mercury, by the density of mercury, 13.595 at 0°, and the acceleration of gravity, 980.7 cm per second per second. The pressure in dynes per square centimeter multiplied by the volume in milliliters gives the work in ergs. Ergs in turn are converted into joules by dividing by 10^7.

Then,

$$R = \frac{pV}{T} = \frac{76.00 \times 13.595 \times 980.7 \times 22{,}414}{273.16 \times 10^7}$$

$$= 8.314 \text{ joules degree}^{-1} \text{ mole}^{-1} \qquad (4)$$

* The discovery of these laws and their combination are described by Roseman and Katzoff, *J. Chem. Education*, **11**, 350 (1934).

† C = centigrade scale; K = absolute temperature scale. $T°$ K = $t°$ C + 273.16°. In this book as in much of the literature $T°$ K is often taken as $t°$ C + 273.1°. If the scale is not specified, it is assumed that the centigrade scale is meant.

‡ A negative exponent signifies division, whereas a positive exponent signifies multiplication. The expression degree^{-1} is equivalent to the expression "per degree."

Joules may be changed into calories by dividing by the conversion factor 4.184 absolute joules per calorie.

$$R = \frac{8.314}{4.184} = 1.987 \text{ cal degree}^{-1} \text{ mole}^{-1} \qquad (5)$$

In calculations involving the gas laws it is usually convenient to express R in liter-atmospheres; in electrochemical problems involving volts and coulombs R is best expressed in joules; and in thermochemical and thermodynamical problems R usually is given in calories. It is necessary to be thoroughly familiar with the different constants and to know which units to use in a specified problem and how to convert one into another.

The Avogadro Law. According to Avogadro's law proposed in 1811, equal volumes of gases at the same temperature and pressure contain the same number of molecules. This law provided a sure foundation for the determination of molecular weights, and it has played an important part in the development of physical chemistry. The simple gas law, $pV = RT$, follows naturally from this law, because, if 1 mole of any gaseous substance contains the same number of molecules, and these, in turn, exert no specific influence on each other, the relations involving volume, pressure, and temperature should be the same for all ideal gases and approximately the same for real gases.

The actual number of molecules in a gram molecule or mole has been determined accurately in many different ways which are entirely independent of each other, and the agreement is excellent. This number, 6.02×10^{23} molecules per mole (that is, per gram molecule) is called the *Avogadro constant*, and it is a fundamental constant of physical chemistry which has many important applications. The experiments on which the value of this constant is based are described in later chapters.

Perrin determined the constant from observation of the random motion of small particles; Rutherford, from a determination of the charge on the alpha particle from radium; Boltwood and Curie, by direct counting of alpha particles and by measurement of the volume of helium resulting from them; and Planck, from an experimental determination of the constants of radiation.

One of the most accurate values is based on Millikan's classical oil-drop experiment in which the charge on the electron was determined. The best value* at present is 6.023×10^{23} and is obtained from studies of crystals with X rays.

* This value, together with the best values of other fundamental constants, is given on page 699.

The weight of a single atom or molecule is obtained by dividing the respective atomic or molecular weight by the Avogadro constant. For example, the weight of an atom of hydrogen is $1.008/6.02 \times 10^{23} = 1.67 \times 10^{-24}$ g; and the weight of a molecule of hydrogen chloride is $36.46/6.02 \times 10^{23} = 6.06 \times 10^{-23}$ g.

Gas Density and Molecular Weight. The density of a gas is defined in physical chemistry as the weight in grams of 1 liter. The densities are useful in calculating molecular weights. According to Avogadro's law, it should be possible to determine the molecular weight of a gaseous substance by weighing a mole of the gas and comparing it with the weight of a mole of some other gas of known molecular weight taken as a standard. Since oxygen has been taken as the standard of atomic weights and assigned an atomic weight of 16, and since there are two atoms in a molecule of oxygen the molecular weight of gaseous oxygen is taken as a standard of 32.

It has been found that at standard conditions, namely, at 0° and 760 mm pressure of mercury, 32 g of oxygen occupies a volume of 22.414 liters after correction for the deviation from the ideal-gas laws. To determine the molecular weight of a gas it is only necessary then to find the weight of 22.414 liters of the gas at 0° and 760 mm of pressure and to make minor corrections for the departure of the gas from the behavior of an ideal gas. A mole of gas is too large to weigh accurately but a measurement may be made on a smaller quantity at any pressure and temperature and converted to the weight of a mole under standard conditions, using the simple gas law.

For example, if g grams of a gas is taken instead of M grams (M being the molecular weight in grams), then, g/M represents the number of moles taken, which is defined in equation 1 as n. Then,

$$pv = nRT = \frac{g}{M}RT = \frac{g}{M}0.08205T \tag{6}$$

In using this equation, since R is given in liter-atmospheres, it is necessary to convert the pressure p into atmospheres and the volume v into liters.* If the pressure is expressed in millimeters of mercury, the value must be divided by 760. With this formula, any one of the quantities, pressure, volume, and temperature, can be readily calculated when all the others are known.

* In physical-chemical calculations it is always necessary to be sure that the quantities entering a formula are expressed in the correct units.

Example 1. Calculate the volume occupied by 10 g of carbon dioxide at 740 mm pressure and 30° if it is assumed that the ideal-gas law holds.

$$v = \frac{gRT}{pM} = \frac{10}{(\frac{740}{760})44.01} \times 0.08205 \times 303.1 = 5.80 \text{ liters}$$

In the *Regnault method* for determining the molecular weight of a gas, a glass bulb is weighed when completely evacuated and again when filled with the gas. The volume is obtained by weighing it when filled with water. A second bulb of the same size is used as a counterpoise to avoid troublesome corrections for air buoyancy and moisture. Exact weighing of large bulbs is difficult.

The work of Baxter and Starkweather † is a classic example of the use of this method. These authors weighed five samples of gas in two different 2-liter globes with an average reproducibility of 3×10^{-5} of the weight of the gas content.

The *Victor Meyer method* is convenient for the approximate determination of molecular weights of substances that can be weighed in the liquid state, thus avoiding the weighing of large vessels. A weighed quantity of liquid in a glass bulblet is evaporated in an air-filled tube heated to a constant temperature. An equivalent volume of air is driven out and measured with a gas buret at known pressure and temperature.

Example 2. In a Victor Meyer apparatus the evaporation of 0.0845 g of liquid ethanol (C_2H_5OH) expelled 45.3 ml of air as measured in a mercury buret at 21.5° and 741 mm. What is the molecular weight of ethanol calculated from these data?

$$M = \frac{gRT}{pv} = \frac{0.0845 \times 0.08205 \times 294.6}{\frac{741.0}{760.0} \times 0.0453} = 46.3$$

The molecular weights calculated by equation 6 are usually too high (often by 1 or 2 per cent) because most gases show deviations from the simple gas law. More exact calculations can be made, as is shown presently; but an approximate value of the molecular weight is sufficient to enable one to choose between the formula weight, obtained by chemical analysis, and some simple multiple of it. For example, even a rough determination is sufficient to distinguish among C_3H_5O, $C_6H_{10}O_2$, or $C_9H_{15}O_3$.

Behavior of Real Gases. Whereas the behavior of ideal or perfect gases is given exactly by the simple relation, $pV = RT$, the behavior of most real gases, especially at high pressures or low temperatures, can be described only with more complicated formulas.

† Baxter and Starkweather, *Proc. Natl. Acad. Sci. U. S.*, **12**, 703 (1926).

This situation is frequently encountered in the development of physical chemistry. It is often necessary to start with the formulation of simple laws which apply strictly only to idealized systems; then, the actual systems are investigated and deviations from the ideal behavior measured and fitted by mathematical formulas; and, finally, the causes of the deviations are explained.

Pressure-volume data for three common gases at 0° are shown in Table I, where the pressure p is given in atmospheres, and the volume V in liters occupied by 1 mole. If the gases were ideal and the simple gas law applicable, the product of pressure and volume should be equal at all pressures to 22.414 liters. The table shows that this product (pV) is far from being constant and that it varies greatly for different gases. Even at 1 atm there is a slight departure from the behavior of a perfect gas.

TABLE I

PRESSURE–VOLUME RELATIONS OF GASES AT 0° [1]

p	Hydrogen		Oxygen		Carbon Dioxide	
	V	pV	V	pV	V	pV
1	22.428	22.43	22.393	22.39	22.262	22.26
50	0.4634	23.17			0.04675	2.338
100	0.2386	23.86	0.2075	20.75	0.04497	4.497
200	0.12712	25.42	0.10234	20.47	0.04285	8.571
300	0.09004	27.01	0.07184	21.55	0.04152	12.46
400	0.07163	28.65	0.05887	23.55	0.04051	16.21
600	0.05318	31.91	0.04736	28.42	0.03894	23.36
800	0.04392	35.13	0.04207	33.66	0.03779	30.23
1000	0.03837	38.37	0.03886	38.86	0.03687	36.87

[1] Volume in liters; pressure in atmospheres.

The influence of higher pressures is brought out clearly in **Fig. 4** where pV is plotted against pressure extending out to high pressures. A low value of pV indicates that the gas is more compressible. All gases show a minimum in a pV curve unless the temperature is too high. Hydrogen and helium, which have very low boiling points, exhibit this minimum only at temperatures much below 0°.

The departure from ideal behavior is brought out still more clearly by plotting pV/RT against pressure, as is done for nitrogen in **Fig. 5.** The influence of temperature as well as pressure on the departure from

ideal behavior is then obvious. The values of pressure, volume, and temperature are determined experimentally. For a perfect gas pV/RT should have a value of unity under all conditions. The behavior of nitrogen is typical of all gases. It is more compressible than a perfect gas at low pressures and less compressible at high pressures; and the departure from ideal behavior becomes less at high temperatures and low pressures where the molecules are kept farther apart.

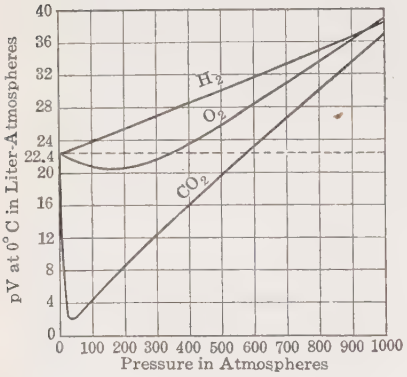


Fig. 4. Influence of high pressures on the product of pressure and volume for typical gases.

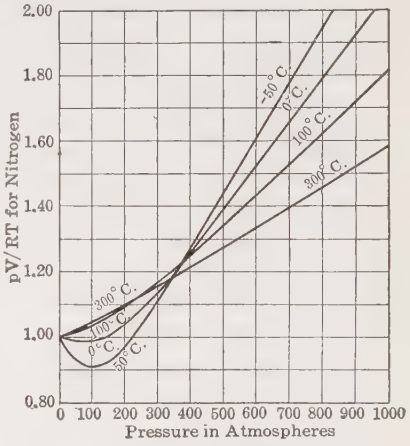


Fig. 5. Influence of high pressures on the quantity pV/RT for nitrogen.

The Critical Temperature. At sufficiently low temperatures a gas may be made to liquefy by applying pressure, thus reducing the volume and bringing the molecules close enough together so that the attractive force between them will be effective. All gases have been liquefied in this way. However, there is a temperature above which it is impossible to liquefy the gas no matter how great a pressure is applied. This temperature is called the *critical temperature;* and the minimum pressure necessary to bring about liquefaction at the critical temperature is called the *critical pressure.* The volume occupied by a mole of gas or liquid at the critical temperature and pressure is called the *critical volume.*

The significance of the critical temperature is shown in **Fig. 6** in which pressure is plotted against volume for 1 mole of carbon dioxide at the several temperatures indicated on the graph.

Lines on a graph which refer to a specified constant temperature are called *isothermals.* At 48.1° the pressure-volume curve is a reciprocal curve similar to that shown in Fig. 1 for an ideal gas. At 35.5° there is

a nick in the curve showing that in the neighborhood of a pressure of 82 atm the gas is deviating considerably from the behavior of an ideal gas and the molecules are close enough to exhibit some attraction for each

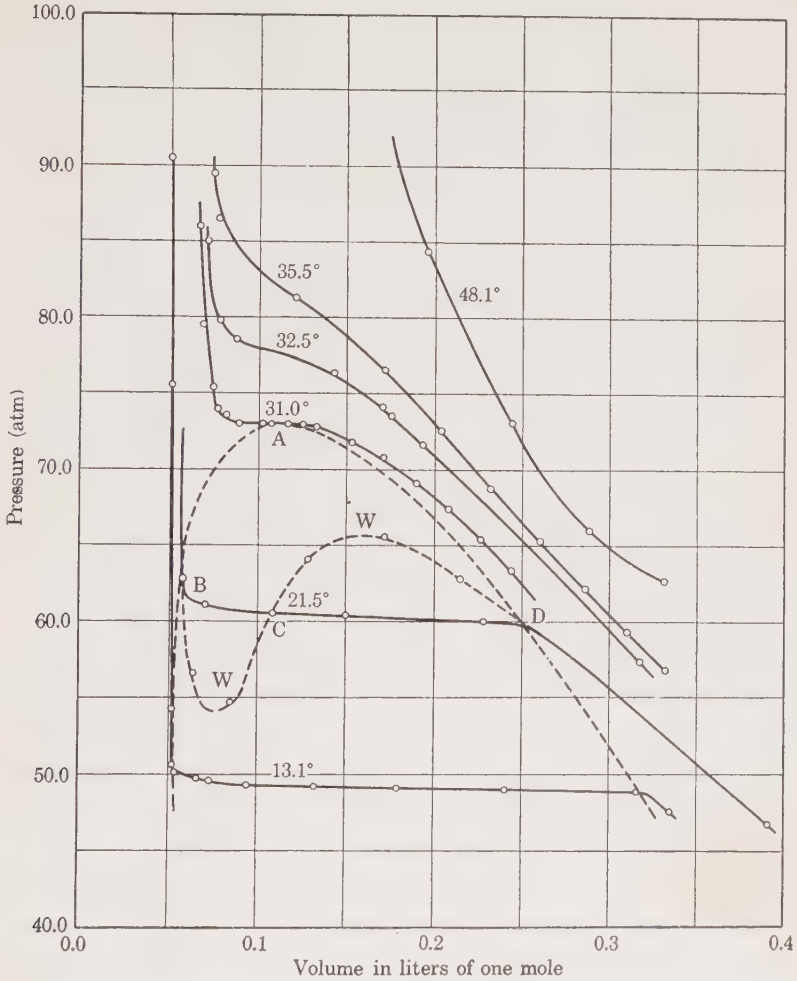


FIG. 6. Pressure–volume curves for carbon dioxide showing the critical temperature and pressure. Van der Waals' calculation shown at *W*.

other, thus making the over-all volume of the gas smaller than that of an ideal gas in which no such attraction exists.

At all temperatures below 31.0° the curves exhibit theoretically horizontal sections as shown by isothermals at 21.5° and 13.1°. These horizontal lines indicate that an infinitesimal increase in pressure causes a

very large decrease in volume, owing to the fact that the gas is liquefying. At the right of the diagram gas alone is present, and the curves follow the simple-gas law approximately; at the extreme left liquid alone is present, and since the liquid is much less compressible than a gas, the curve is steeper than that for the gas. Along the straight horizontal part of the curve both gas and liquid exist together. This region in which gas and liquid are coexistent is enclosed by the dotted line, the maximum point A of which gives the critical temperature, critical pressure, and critical volume. The wavy line W is discussed on page 17.

TABLE II

Critical Constants and Boiling Points of Gases

Gas	T_{BP} (°K)	T_c (°K)	$T_{BP}{}^1/T_c$	p_c (atm)	V_c (ml/mole)	$T_{MP}{}^1$ (°K)	RT_c/p_cV_c
He	4.2	5.2	0.81	2.25	61.5	0.9	3.08
H_2	20.4	33.2	0.61	12.8	69.7	14.0	3.05
N_2	77.3	126.0	0.61	33.5	90.0	63.2	3.42
CO	81.1	134.4	0.60	34.6	90.0	66.1	3.54
A	87.4	150.7	0.58	48.0	77.1	83.9	3.35
O_2	90.1	154.3	0.58	49.7	74.4	54.7	3.42
CH_4	111.7	190.2	0.59	45.6	98.8	89.1	3.47
NO	122.1	177.1	0.69	64	57.2	112.1	3.97
C_2H_4	169.3	282.8	0.60	50.5	126	103.7	3.64
HCl	188.1	324.5	0.58	81.6	87	162.1	3.75
C_2H_2	189.5	308.6	0.61	61.6	113	191.3	3.64
CO_2	194.6	304.2	0.64	72.8	94.2	.....	3.64
H_2S	213.5	373.5	0.57	88.9	.....	190.2	....
Cl_2	238.5	417.1	0.58	76.1	123	171.5	3.64
NH_3	239.7	405.5	0.59	112.2	72.0	195.4	4.12
SO_2	263.1	430.2	0.61	77.6	125	200.4	3.64
n-C_6H_{14}	342.1	507.9	0.67	29.6	367	178.8	3.83
CCl_4	349.9	556.2	0.63	45.0	276	250.1	3.68
C_2H_5OH	351.6	516.2	0.68	63.0	167	155.8	4.02
C_6H_6	352.7	561.6	0.63	47.9	256	278.6	3.76
H_2O	373.1	647.3	0.58	217.7	56.6	273.1	4.39
n-C_7H_{16}	371.5	540	0.69	27.0	416	183.1	3.95
CH_3COOH	391.2	594.7	0.66	57.1	171	289.7	4.99
n-C_8H_{18}	397.7	570	0.70	24.7	490	216.6	3.86
Hg	630.0	1735	0.36	1042	40.1	234.2	3.40

[1] The melting points T_{MP} and ratios of boiling point to critical temperature T_{BP}/T_c given in these columns are not involved in the present discussions but are included for reference in a later chapter.

All gases give curves similar to those shown in Fig. 6 and exhibit critical temperatures below which it is possible to produce liquefication by application of sufficient pressure.

In Table II the critical temperatures T_c, pressures p_c, and volumes V_c are given for several of the common gases, arranged in order of increasing boiling points.

Several of the substances given in the table are liquids at room temperature, but they become gaseous at sufficiently high temperatures. Gases which are below their critical temperatures are often called vapors. The pressure–volume–temperature relations are approximately the same for all gases, and, since at the critical temperatures the liquids become indistinguishable from the corresponding gases, the p–V–T relations for all liquids should be the same if the liquids are compared at their critical temperatures. That this relation holds approximately is seen by examination of the last column where the value of RT_c/p_cV_c is found to be about 3.5 for many substances. With the exception of a few liquids such as water, ammonia, alcohols, and organic acids, which are abnormal as explained in a later chapter, this value varies from 3 to 4 over a range from 4° to 630° K.

Equation of van der Waals. Van der Waals in 1879 made an early attempt to introduce additional terms into the simple gas equation and thus give an expression which describes more exactly the behavior of real gases. An examination of Figs. 4 and 5 reveals the fact that at low pressures real gases may be more compressible than an ideal gas and that at high pressures they may be less compressible. The tendency to be more compressible is due to the fact that the molecules have some attraction for each other and tend to draw together. The tendency to be less compressible is probably due to the fact that the molecules of the gas are less compressible than the gas itself, and the volume of the molecules themselves becomes an appreciable part of the total volume when the pressure becomes high and the total volume small.

Van der Waals put these ideas into a general equation as follows:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad (7)$$

The constant a expresses the fact that a force of attraction exists between two molecules of the gas. The total forces exerted between two small neighboring regions of gas will depend on the number of molecules in the region. The larger the volume holding 1 mole of gas, the fewer are the molecules in a given region and the less the attraction.

The attraction from one region then varies inversely as the volume, and in the other region it also varies inversely as the volume. The total attraction between two small regions then is inversely proportional to the product of the two, that is, to V^2.

Since the force of this attraction a/V^2 augments the pressure in tending to make the volume small, it is added to the term p.

The term b is connected with the volume of the molecules themselves, and so it is subtracted from the total volume V to give an effective compressible volume. The volume b appears to have a value about four times the volume occupied by the molecules themselves if they are considered to be simple spheres.

When V is large both b and a/V^2 become negligible; and the van der Waals equation reduces to the simple gas equation, $pV = RT$. In general, all gases tend to become ideal at low pressures and approach the behavior given by the simple gas law, $pV = RT$.

Van der Waals' constants for a few additional gases are listed in Table III.* They can be calculated from physical-chemical measurements as shown later on page 18.

TABLE III

VAN DER WAALS' CONSTANTS

Units: liters, atmospheres, moles, degrees absolute

Gas	a (liter^2 atm mole^{-2})	b (liters mole^{-1})	Gas	a (liter^2 atm mole^{-2})	b (liters mole^{-1})
C_2H_2	4.390	0.05136	CO	1.485	0.03985
NH_3	4.170	0.03707	Cl_2	6.493	0.05622
C_6H_6	18.00	0.1154	H_2	0.2444	0.02661
CH_4	2.253	0.04278	HCl	3.667	0.04081
CO_2	3.592	0.04267	O_2	1.360	0.03183
C_2H_6	5.489	0.06380	SO_2	6.714	0.05636
C_2H_4	4.471	0.05714	N_2	1.390	0.03913
He	0.03412	0.02370	H_2O	5.464	0.03049
NO	1.340	0.02789	NO_2	5.284	0.04424

The values of a are given here in liter^2 atm mole^{-2}, but sometimes they are expressed in cc instead of liters giving cm^6 atm mole^{-2}. The values of b also are sometimes given in cm^3 per mole instead of liters per mole.

* Lange, "Handbook of Chemistry," Handbook Publishers, Sandusky, Ohio, 1941.

Example 3. Calculate the pressure exerted by a mole of sulfur dioxide in 10 liters at 100° using (*a*) the ideal-gas law and (*b*) van der Waals' equation.

$$(a)\quad p = \frac{nRT}{V} = \frac{1 \times 0.08205 \times 373.1}{10.00} = 3.061 \text{ atm}$$

$$(b)\quad p = \frac{RT}{V - b} - \frac{a}{V^2} = \frac{0.08205 \times 373.1}{10.00 - 0.0564} - \frac{6.714}{100.0}$$

$$= 3.177 \text{ atm}$$

The attractive force between molecules which gives rise to the term a/V^2 in van der Waals' equation, is responsible not only for the deviations from the gas laws at ordinary pressures but also for the condensation of gases to liquids, for certain types of solubility, and for many physical and chemical phenomena. It is electrical in character; for, although the molecules are uncharged, they contain within them positive and negative parts which can induce electric charges in a neighboring molecule, and these charged parts of molecules then attract oppositely charged units in their vicinity and tend to bring the molecules closer together.

Van der Waals' equation has been very successful in expressing the behavior of gases at atmospheric pressure and up to a few atmospheres, but it is inadequate for calculating the properties of gases under high pressures. It has been useful in the theoretical studies of the behavior of gases.

There is an interesting relationship between the van der Waals constants, a and b, and the critical constants T_c, p_c, and V_c. Multiplying out the terms in van der Waals' equation 7 and rearranging in descending powers of V, we have

$$V^3 - V^2\left(b + \frac{RT}{p}\right) + V\frac{a}{p} - \frac{ab}{p} = 0 \qquad (8)$$

This cubic equation has three possible solutions, each value of p giving three corresponding roots of V. The terms, a, b, R, and T, are constants. This equation is shown graphically by the dotted line W on the 21.5° isothermal in Fig. 6 where the three values are evident as three intersections B, C, and D on the horizontal line corresponding to a fixed value of the pressure. This dotted calculated line then appears to give a continuous transition from the gaseous phase to the liquid phase, but in reality the transition is abrupt and discontinuous, both liquid and vapor existing as indicated along the straight horizontal lines. This theoretical dotted line $DWCWB$ does not correspond to normal physical conditions; for example the slope of the curve at C is positive, a fact which would

lead to the unnatural condition that an increase in pressure produces an increase in volume. However, it is possible to supersaturate the vapor and have pressures of gas in an unstable condition represented by the beginning of the dotted line DW, before the vapor has a chance to liquefy and bring the pressure down to that of the horizontal line. At the critical temperature (31.1° for carbon dioxide) all three values of V obtained by solving equation 8 take on real values, and all are the same and equal to the critical volume. In terms of the graph the three values of V coincide in a point A, the critical volume.

It can be shown by solving equation 8 (appendix, page 672) that $a = 3p_cV_c^2$, that $b = V_c/3$ and that $R = \frac{8}{3}(p_cV_c/T_c)$, where p_c, V_c, and T_c are the values at the critical point. In fact this is one of the ways of evaluating van der Waals' constants a and b.

If, in the equation of van der Waals, the values of p, V, and T are expressed as fractions α, β, and γ of the corresponding critical values, then $p = \alpha p_c$; $V = \beta v_c$; and $T = \gamma T_c$. Substituting these values of p, V, and T into van der Waals' equation 7 gives

$$\left(\alpha p_c + \frac{a}{(\beta v_c)^2}\right)(\beta v_c - b) = R\gamma T_c$$

and, again substituting the values of a, b, and R just given into this equation, we have

$$\left(\alpha + \frac{3}{\beta^2}\right)(3\beta - 1) = 8\gamma \qquad (9)$$

In equation 9, sometimes called a reduced equation of state, everything connected with the individual nature of the substance has vanished, thus making it theoretically applicable to all substances in the liquid or gaseous state in the same way that the fundamental gas equation is applicable to all gases, irrespective of their specific nature. This equation is only a rough approximation and does not apply at all satisfactorily to liquids. It is useful, however, in pointing out that, when nonideal gases are compared, not at equal temperatures, but at temperatures which are equal fractions of their critical temperatures, some of the properties due to the specific chemical nature of the gas will disappear, and the comparisons of physical properties will be more significant.

Other Equations of State. An equation which gives the relations among the pressure, volume, and temperature of a gas is called an equation of state. The equation of van der Waals is mathematically inconvenient to use in certain types of problems because it involves the solving

of a cubic equation. The following equation, developed by Berthelot, is useful at moderate pressures:

$$pv = nRT\left[1 + \frac{9}{128}\frac{p}{p_c}\frac{T_c}{T}\left(1 - 6\frac{T_c^2}{T^2}\right)\right] \tag{10}$$

In this equation p_c is the critical pressure and T_c the critical temperature (page 14). Inspection of the equation shows that, as T increases or as p decreases, it approaches the simple equation $pv = nRT$ expressing the behavior of an ideal gas. The values of the ratio pv/RT calculated by means of this equation agree closely with those determined experimentally, provided the gases are neither associated nor dissociated and are sufficiently removed from their liquefaction temperature and pressure.

Other empirical equations of state * are necessary to meet the demands for greater accuracy in industrial chemistry where catalytic reactions are carried out under high pressure. They involve more constants and are more cumbersome to use. The Beattie–Bridgman equation with five constants, given in the appendix on page 673, is among the more exact equations for use at high pressures.

According to another equation, known as the virial equation, the deviation from the behavior of an ideal gas at a given temperature is a function of the pressure as shown in the following equation.

$$pV = RT + Bp + Cp^2 + \cdots \tag{11}$$

where the constants B, C $\cdots$ are evaluated from experimental p–V–T data. The most important constant B can be connected with certain physical and chemical properties of the gas. This equation is finding increasing application in both theoretical and practical work.

The chart shown in **Fig. 7** developed by Hougen and Watson † takes advantage of the simplifications introduced by expressing the temperature and pressure as fractions of the critical values and permits one to calculate easily the p–V–T relations for any gas when the critical temperature and pressure are known. It is particularly valuable for calculations at high pressures when other data for the equations of state are not known. In this chart the expression pV/RT sometimes called the compressibility factor, is plotted against the reduced pressure p/p_c for different reduced temperatures T/T_c. Large charts accurately drawn with more values of the reduced temperatures are available.

* Woolsey, *J. Chem. Education*, **16**, 60 (1939).

† Hougen and Watson, "Industrial Chemical Calculations," John Wiley & Sons New York, 1946.

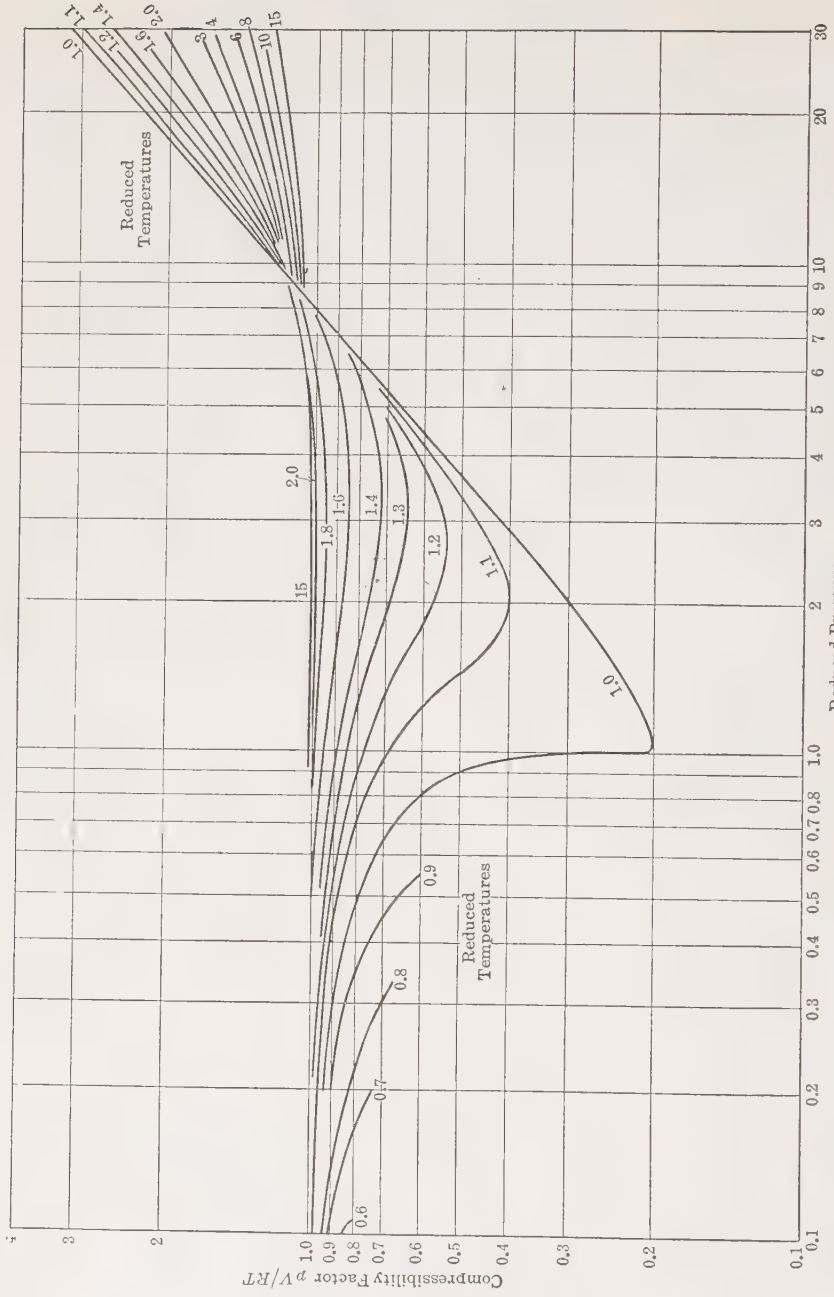


FIG. 7. Hougen and Watson chart for calculating pressure, volume, and temperature relations at high pressures.

Example 4. With the Hougen and Watson chart, estimate the volume occupied by a mole of oxygen at −88° C and 44.7 atm. The critical temperature and pressure are found in Table II.

$$\frac{T}{T_c} = \frac{273.1 - 88.0}{154.3} = 1.20; \quad \frac{p}{p_c} = \frac{44.7}{49.7} = 0.90$$

From the chart, $pV/RT = 0.80$.

$$V = \frac{0.80RT}{p} = \frac{0.80 \times 0.08205 \times 185.1}{44.7} = 0.272 \text{ liter}$$

The different equations of state are compared in Table IV.

TABLE IV

pV/RT FOR NITROGEN AT 1000 ATMOSPHERES

Temperature	Observed	Ideal	Van der Waals	Berthelot	Hougen and Watson Chart
0° C	2.0632	1.0000	2.426	0.731	2.10
50° C	1.9285	1.0000	2.182	1.071	1.95

The decision as to which equation of state should be used depends on the amount of data available and the purpose of the study. If one desires to fit the data with great accuracy over large pressure ranges the virial equation is recommended because of its flexibility. Such an equation is really a condensed summary of the data. It requires a different set of constants for each temperature and it becomes very cumbersome for practical application. The Beattie–Bridgman equation, with five or six adjustable constants, is useful for practical purposes since it can be made to fit the data with reasonable accuracy over a considerable temperature and pressure range, but often it is not exact beyond 200 atm.

For pressures up to a few atmospheres very satisfactory results are obtainable with the equation of van der Waals or Berthelot if the critical temperature and pressure are known. The Hougen and Watson chart gives very good results even up to pressures of several hundreds of atmospheres.

Exact Molecular Weights. When values of the molecular weights more exact than those obtainable by the simple gas-law calculation are necessary, determinations may be made at lower and lower pressures,

usually by the Regnault method. The deviations from the simple gas law become less at the lower pressures and approach zero, but serious experimental difficulties are involved in weighing a large volume of gas at a low pressure. Precise measurements of densities at several low pressures can be used to determine the atomic weights of the elements which make up the molecule, with an accuracy as great as that obtainable by chemical analysis. This method is called the method of limiting densities.

As the pressure decreases, the volume increases, and the weight per liter decreases. The density d defined by g/v decreases; but the ratio of

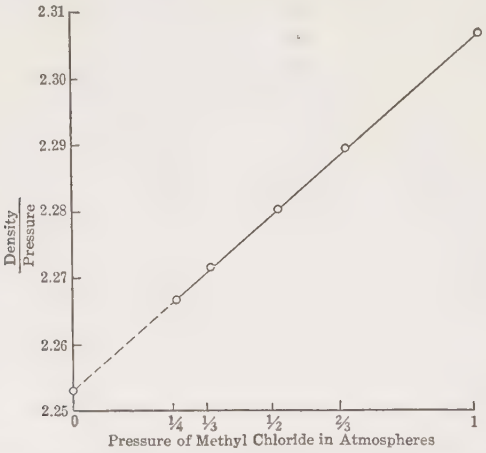


FIG. 8. Determination of molecular weight by extrapolation of density/pressure to zero pressure.

density to pressure d/p or g/vp should remain constant if the gas is perfect, since pv is constant and the total weight g remains unchanged. For ordinary gases, however, the ratio of density to pressure is not constant but decreases as the pressure decreases, as shown in **Fig. 8.**

For permanent gases it has been found that practically a straight line is produced when d/p is plotted against p at pressures below 1 atm. The straight line is extrapolated beyond the region of experimental measurements until it intersects the Y axis where $p = 0$. The intercept can be obtained mathematically from the data without graphing. Gases which liquefy at fairly high temperatures show greater deviations, and the straight-line relation does not hold. More complicated mathematical formulas may then be necessary for the extrapolation.*

Since the deviations from the ideal-gas law approach zero as the

* Birge and Jenkins, *J. Chem. Phys.*, **2**, 167 (1934).

pressure is reduced, the exact molecular weight M is given by the equation,

$$M = \left(\frac{d}{p}\right)_0 RT \tag{12}$$

where $(d/p)_0$ is the ratio of density to pressure extrapolated to zero pressure.

Example 5. Calculate the molecular weight of methyl chloride and the atomic weight of chlorine from the following data, having given the atomic weights of carbon and hydrogen:

Pressure, atmospheres	1	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$
Density at 0°, grams per liter	2.3074	1.5263	1.1401	0.75713	0.56660

The extrapolated ratio of density to pressure at 0° is 2.2528 as shown in Fig. 8.

Then $M = 2.2528 \times 0.082054 \times 273.16 = 50.495$.

If we subtract from 50.495 the atomic weight of carbon, 12.010, and three times the atomic weight of hydrogen, 3.024, a value of 35.461 is obtained for the atomic weight of chlorine. The accepted value is 35.457.

Exact molecular weights can be obtained with the help of Berthelot's equation or other suitable equations of state, and they are sufficiently accurate to be used for the calculation of atomic weights over limited ranges.

Example 6. Calculate the atomic weight of nitrogen from the fact that the density of nitric oxide, NO at 0° and 760 mm is 1.3402 g per liter. The critical constants are 177.1° K and 64 atm.

Calculating the molecular weight M by Berthelot's equation gives

$$M = \frac{gRT}{pv}\left[1 + \frac{9}{128}\frac{p}{p_c}\frac{T_c}{T}\left(1 - 6\frac{T_c^2}{T^2}\right)\right]$$

$$= \frac{(1.3402)(0.082054)(273.16)}{1 \times 1}\left[1 + \frac{9}{128}\frac{1}{64}\frac{177.1}{273.16}\left(1 - 6\frac{177.1^2}{273.16^2}\right)\right]$$

$$= 30.039[1 - 1.12 \times 10^{-3}] = 30.005$$

The atomic weight of nitrogen = 30.005 − 16.000 = 14.005. The accepted atomic weight of nitrogen is 14.008. In calculations of this type when the correction term is small, it is sufficient to calculate the correction term approximately with a slide rule.

Abnormal Densities. The molecular weights of a great many substances have been determined by measurements of the density of the gas. Generally, they agree with the molecular weights obtained from

the sum of the atomic weights. Difficulty, however, was encountered with a few substances whose molecular weights seemed abnormal. The experimental results were in error, Avogadro's hypothesis was not universally applicable, or some new phenomenon was entering in. This situation arises frequently in the development of science. Exceptions to a general law are found, and for a time the fate of the whole law is uncertain. More exact experiments or slight corrections (such as were shown for the gas law) may save the law, or perhaps it may have to be discarded or modified. In these cases the difficulty was traced to the fact that some of the gases dissociated or broke down into smaller units or that they associated into multiples of the molecular weight.

The molecular weight of sulfur below 500° * corresponds to the formula S_8; at 1100° it corresponds to S_2; and at intermediate temperatures it may correspond to S_4 or S_6 or a mixture of the various forms. Iodine gives I_2 from 200 to 600°; but at 1400°, and above, it has half the density and corresponds to monatomic molecules. At intermediate temperatures all densities between these two values can be obtained. Arsenic oxide, aluminum chloride, phosphorus chloride, ammonium chloride, and various other substances dissociate in a similar manner, particularly at high temperatures.

Decreasing molecular weights at higher temperatures are due to dissociation of the molecules into smaller molecules. Since the original materials are obtained on cooling, the breaking down into parts must be reversible. One of the earliest substances to be studied in this connection was ammonium chloride. It was suspected that the low molecular weight was occasioned by the reaction.

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

the ammonia and hydrochloric acid at the high temperature occupying twice the volume of ammonium chloride vapor and giving half the density, when dissociation was complete. This interpretation was proved to be correct when it was shown that the heated vapor contained an alkaline gas NH_3 and an acid gas HCl which could be separated by fractional diffusion through a porous plug of solid ammonium chloride. The gas diffusing through the plug turned litmus paper blue. It is shown on page 28 that gases of low molecular weight diffuse more rapidly than those of high molecular weight.

Use is made of these experimentally measured densities in calculating quantitatively the extent of the dissociation of the heavier molecules into lighter ones, as shown on page 259.

* As already explained, centigrade scale is meant unless otherwise specified.

The Kinetic Theory. According to the kinetic theory, the molecules and atoms of any substance are in a constant state of motion at all temperatures above absolute zero. When heat is supplied to any material, for example, by contact with a warmer body, by a chemical reaction, or by absorption of radiation, the molecules move faster, and the temperature rises, unless prevented by some other heat-absorbing process. The molecules are restricted in their movement by attractive forces which hold them near a fixed position in solids and, to a lesser extent, in liquids, so that the motion corresponds to a molecular vibration rather than to a flow of matter. As the temperature increases, the vibrations in the solid or liquid become more vigorous until finally the kinetic energy of the fastest-moving molecules is sufficient to cause the molecules to break away from the other molecules and enter the gaseous state—that is, the substance vaporizes.

The molecules in the gas thus formed do not vibrate in the neighborhood of a point as they did before, but they are completely separated from each other and move in straight lines with an average velocity which increases as the temperature of the gas increases. The volume occupied by the molecules of the gas themselves is much smaller than the volume of the containing vessel which they fill, and, accordingly, a molecule moves for considerable distances before it collides with one of its neighbors. The average distance through which the molecules move between collisions is called the *mean free path.*

The combined effect of the impacts of the molecules on the walls of the containing vessel accounts for the pressure exerted by the gas. When these walls are moved outward by a gas and the gas expands against an external pressure, it does work at the expense of the kinetic energy of its molecules. If the gas is insulated, this loss of kinetic energy will slow down the motion of the molecules and produce a cooling effect, but, if it is in good thermal contact with its surroundings, heat will flow in and offset the loss of kinetic energy so that the temperature remains constant.

The molecules of a gas undergo an enormous number of collisions with other molecules, and their direction and velocity is constantly changing in a random manner. The distribution of velocities in a group of molecules has been determined mathematically by Maxwell and Boltzmann and used in a number of different calculations, as discussed later on pages 368 and 678. In the present chapter the kinetic theory is used with simplifying assumptions to develop a simple equation which is important in describing the quantitative behavior of gases.

Referring to **Fig. 9,** we may imagine that in this cube, which has a length of l centimeters, there are n molecules each having the mass m.

The temperature of the gas remains constant. We will assume that the molecules are very small compared with the distances between them, that there are no forces of attraction between the molecules, and that the collisions of the molecules with each other and with the sides of the box are perfectly elastic (that is, that no energy is used up inside the molecule by rearrangements of its parts). The molecules are moving with widely different velocities but we may take one velocity as characteristic of all the molecules at the specified temperature of the imaginary experiment. We might take the average velocity, but it will be remembered from experiments in physics on the resolution of forces that it is more significant to use the root-mean-square velocity. In the present case the root-mean-square velocity is the square root of $1/n$th of the sum of the squares of the individual velocities of all the n molecules.

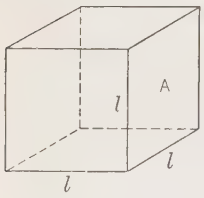


FIG. 9. Imaginary cube used in the derivation of the kinetic equation, $pv = \frac{1}{3}mnu^2$.

As a result of their collisions with each other inside the box, the molecules will be moving sometimes in one direction, sometimes in another; since these directions may be resolved along three different axes at right angles to each other, it may be supposed that one third of the molecules are moving always in the direction perpendicular to the wall A.

Considering the collisions of molecules with A, a molecule will strike A every $2l$ centimeters as it moves back and forth across the box. If its velocity is u centimeters per second, it will collide $u/2l$ times per second with A. Since the collisions are perfectly elastic, the molecule will rebound with velocity $-u$, having suffered no loss in kinetic energy. Since momentum is defined as the product of mass and velocity, the momentum before collision is mu and after collision is $-mu$; so that the change in momentum per collision per molecule is $2mu$. There are $u/2l$ collisions per second; so the change in momentum per molecule per second is mu^2/l. The total change in momentum per second for the $n/3$ molecules which can collide with A is $\frac{n}{3}\frac{mu^2}{l}$; this represents the average force on A, since force may be defined as the change in momentum per second. Pressure is force per square centimeter, and so the pressure p on the area A, or l^2, is

$$p = \frac{\text{force}}{\text{area}} = \frac{n}{3}\frac{mu^2}{l}\frac{1}{l^2} \tag{13}$$

But the volume v of the box is l^3, and we have

$$p = \frac{n}{3}\frac{mu^2}{v} \tag{14}$$

or

$$pv = \tfrac{1}{3}nmu^2 \tag{15}$$

This is the fundamental equation of the kinetic theory of gases which finds frequent application in physical chemistry. It is not restricted to gases in a cubical vessel, because any vessel may be considered to be made up of a large number of small cubes for each of which this derivation applies. It must be remembered, however, that the equation applies strictly only to ideal gases in which there is no attraction between the molecules and no internal loss of energy on collision. It can be applied, however, with fair accuracy to most real gases.

Equation 15 may be rewritten in the form,

$$pv = (\tfrac{2}{3})\tfrac{1}{2}nmu^2 = \tfrac{2}{3} \text{ total kinetic energy} \tag{16}$$

since the kinetic energy of a moving body is $\frac{1}{2}mu^2$. Inasmuch as the kinetic energy of the molecules depends on the temperature, it will remain constant at constant temperature. According to equation 16 then pv is constant at constant temperature—and we have thus derived Boyle's law.

An expression may be deduced also from the fundamental kinetic equation which is equivalent to Avogadro's law.

For one gas,

$$pv = \tfrac{1}{3}n_1m_1{u_1}^2$$

and for another gas of different molecular weight,

$$pv = \tfrac{1}{3}n_2m_2{u_2}^2$$

so

$$\tfrac{1}{3}n_1m_1{u_1}^2 = \tfrac{1}{3}n_2m_2{u_2}^2 \tag{17}$$

At the same temperature the kinetic energies are assumed to be equal:

$$\tfrac{1}{2}m_1{u_1}^2 = \tfrac{1}{2}m_2{u_2}^2 \tag{18}$$

If equation 17 is divided by equation 18, several quantities cancel out, and we have

$$n_1 = n_2 \tag{19}$$

This equation shows that, at equal temperatures, pressures, and volumes, the number of molecules in each gas is the same—provided that the gases are ideal and that the conditions assumed in the derivation of equation 15 apply.

Velocity of Molecules. If the fundamental kinetic equation is solved for u and the molar weight M is equal to mn, we have

$$u = \sqrt{\frac{3pv}{mn}} = \sqrt{\frac{3RT}{M}} \tag{20}$$

Example 7. What is the root-mean-square velocity of a molecule of hydrogen at 0°?

$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 273.1 \times 10^7}{2.016}} = 1.84 \times 10^5 \text{ cm sec}^{-1}$$

In this calculation R is taken in ergs per degree per mole in order to have consistent units in the cgs (centimeter–gram–second) system.

It is seen that on the average a hydrogen molecule at 0° travels at a rate faster than a mile per second, but it travels only an exceedingly short distance before colliding with another molecule and starting off in a different direction.

This derivation, like all those depending on the relation $pv = RT$, is exact only for perfect gases. Even if the expression $\sqrt{3pv/mn}$ is used, the answer still may be erroneous (perhaps to about 1 per cent) because in the derivation an ideal gas was assumed with no attraction between the molecules.

Relative rates of diffusion and molecular weights may be estimated from the fundamental kinetic equation. Since the density d of a gas is equal to the mass divided by the volume, $d = mn/v$;

$$u = \sqrt{\frac{3pv}{mn}} = \sqrt{\frac{3p}{d}} \tag{21}$$

If the pressure and temperature of two different gases are the same, the ratio of the root-mean-square velocities u_1 and u_2 may be calculated from the two densities, d_1 and d_2, or from the molecular weights, M_1 and M_2, as shown by equation 20:

$$\frac{u_1}{u_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \tag{22}$$

Under certain conditions the times required for two gases to flow through a small aperture are inversely proportional to the velocities of the molecules and, hence, directly proportional to the square root of the molecular weights. The proportionality is exact if the cross section of the aperture is small compared with the average distance through which a molecule travels before colliding with another molecule. At ordinary

pressures this distance is so small that the conditions are no longer satisfied and a correction term is required, unless both gases happen to be of the same type—both diatomic, for example.

REFERENCES

Loeb, "The Kinetic Theory of Gases," McGraw-Hill Book Co., New York, 1936.
Newitt, "The Design of High Pressure Plant and the Properties of Fluids at High Pressures," Oxford University Press, Oxford, 1940.
Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, 1946, Chapter IV.

PROBLEMS

1. What pressure does a concentration of 1 mole per liter of an ideal gas give in millimeters of mercury at (*a*) 25° and (*b*) 1000°?

Ans. (*a*) 18,590 mm. (*b*) 79,344 mm.

2. How much does a liter of octane gas C_8H_{18} weigh at 150° and 1 atm pressure?

Ans. 3.289 g.

3. How many grams of ammonia will occupy the same volume at −25° as is occupied by 5 g of oxygen at 25° if the pressure is the same? *Ans.* 3.2 g.

4. Estimate the tons of carbon dioxide over a square mile of the earth's surface if the atmospheric pressure is 760 mm and the air contains 0.03 of one per cent of carbon dioxide. *Ans.* 8850 tons.

5. A certain hydrocarbon is found to have a vapor density of 2.550 g per liter at 100° and 760 mm. Chemical analysis shows that the substance contains one atom of carbon to one atom of hydrogen. What is its molecular formula?

Ans. C_6H_6.

6. Calculate the pressure exerted when 1 mole of water is heated in a volume of 10 liters to a temperature of 150°, using (*a*) the simple gas law and (*b*) van der Waals' equation. *Ans.* (*a*) 3.47 atm. (*b*) 3.43 atm.

7. Using van der Waals' equation, calculate the pressure exerted by 1 mole of CO_2 at 0° which has a volume of (*a*) 1 liter, (*b*) 0.05 liter. (*c*) Repeat the calculations at 100° and 0.05 liter. *Ans.* (*a*) 19.82 *atm.* (*b*) 1620 *atm.* (*c*) 2740 *atm.*

8. The density of ammonia in grams per liter was determined at various pressures by weighing the gas in large glass bulbs. The values of d/p (d = density in grams per liter, p = pressure in atmospheres) at 0° were as follows: 0.77169 at 1 atm, 0.76773 at $\frac{2}{3}$ atm, 0.76585 at $\frac{1}{2}$ atm, 0.76383 at $\frac{1}{3}$ atm. What is the limiting value of density per pressure at zero pressure, as determined graphically, and what is the molecular weight of ammonia? If the atomic weight of hydrogen is taken as 1.008, what is the atomic weight of nitrogen? *Ans.* 14.008.

9. Calculate the temperature at which the root-mean-square velocity of a nitrogen molecule is the same as that of a helium molecule at 27°. *Ans.* 2102° K.

10. A 6-to-1 mixture by volume of neon and argon is allowed to diffuse through a small orifice into an evacuated space. What is the composition of the mixture which first passes through? *Ans.* 10.6 per cent A and 89.4 per cent Ne.

---

11. A mixture of 0.1 g of hydrogen and 0.2 g of nitrogen is to be stored at 760 mm pressure and 25°. What must the volume of the container be, if it is assumed that there is no interaction between nitrogen and hydrogen?

12. A 1-liter flask containing an organic vapor at 25° is evacuated to 0.0001 mm (of mercury). How many molecules remain in the flask?

13. (*a*) How many grams of air are there in the atmosphere surrounding the earth, if it is assumed that the earth is a sphere with a diameter of 12 million meters and that the atmospheric pressure is 760 mm everywhere on the surface?

(*b*) How many moles of air are there in the total atmosphere, if it is assumed that the average molecular weight of air is 28.8?

(*c*) How many molecules of oxygen are there in the earth's atmosphere, if one fifth of the air by volume is oxygen?

14. What pressure will be generated if 100 g of methanol CH_3OH is evaporated at 100° in an evacuated vessel having a volume of 2 liters?

15. A certain liquid is weighed out in a Victor Meyer apparatus and vaporized. The weight of liquid is 0.110 g, the pressure 737 mm, and the temperature 25.0°. If the volume of displaced air, collected over mercury, is 22.5 ml, what is the molecular weight of the substance?

16. A certain organic compound weighing 0.716 g gave a volume of 242.6 ml when vaporized at 200° and 750 mm. What is the molecular formula of the substance if chemical analysis shows that it must be C_3H_6O or some multiple of this formula?

17. The following values for the density of nitrogen at 0° have been reported by Baxter and Starkweather:

Pressure in millimeters	760	506.67	253.33
Density in grams per liter	1.25036	0.83348	0.41667

Calculate the atomic weight of nitrogen.

18. (*a*) Give the van der Waals formula for n moles of gas instead of 1 mole.

(*b*) Calculate the pressure exerted by 453.6 g (1 lb) of chlorine in a 10-liter flask at 100°, using the ideal-gas law.

(*c*) Repeat the calculation, using van der Waals' equation.

(*d*) Repeat the calculation, using Berthelot's equation.

19. Calculate from the Hougen–Watson chart the volume of 453.6 g (1 lb) of chlorine at 17.65 atm and 100°, and compare the result with the data of Problem 18.

20. Calculate the root-mean-square velocity of (*a*) carbon tetrachloride molecules and (*b*) ammonia molecules at 100°.

(*c*) How much longer will it take for a millimole of carbon tetrachloride vapor to diffuse out of a small opening than a millimole of ammonia?

(*d*) How much longer will it take for a milligram of ammonia to diffuse out of a small opening than a milligram of carbon tetrachloride vapor?

---

21. One liter of a gas is contained in a balloon at 25° and 1 atm pressure. If the gas is heated to 45°, what must be the applied pressure in order that the volume remain constant?

22. How many molecules of sulfur dioxide are contained in a liter:

(*a*) at 1 atm pressure and 25°?

(*b*) at 1 atm pressure and 1000°?

(*c*) at 1 mm pressure and 25°?

(*d*) at 1 mm pressure and 1000°?

23. In a Victor Meyer experiment 0.2350 g of a liquid is vaporized, and the volume of displaced air measured over water in a gas buret is 40.2 ml at 23.0° and 730 mm. Since the air in the buret has become saturated with water, it is necessary to subtract

the vapor pressure of the water, which is 21.0 mm, from the total pressure. What is the molecular weight of the vaporized material?

24. Convert van der Waals' constant a as given in Table III for ammonia into:

(a) cm^6 atm $mole^{-2}$.

(b) dyne cm^4 $mole^{-2}$.

(c) Convert the corresponding constant b into cm^3 $mole^{-1}$.

25. Four hundred milliliters of an organic vapor weighed 0.5220 g at 27°, and 750 mm. Chemical analysis gave carbon 37.52 per cent; hydrogen 12.56 per cent, and oxygen 49.90 per cent. What is the formula of the organic substance?

26. The ratio of the weight of 1 liter of ethyl chloride to the pressure in atmospheres at three different pressures at 0° is as follows: 2.9002 at 760 mm, 2.8919 at 475 mm, 2.8863 at 285 mm. Calculate the molecular weight of ethyl chloride and the atomic weight of chlorine by the method of limiting densities, taking the atomic weights of carbon and hydrogen as known.

27. The weight of a certain evacuated vessel is found to increase 0.2500, 0.5535, and 0.5268 g when oxygen, chlorine, and a compound of oxygen and chlorine, respectively, are separately admitted into the vessel under the same conditions of temperature and pressure. Calculate from these data alone the molecular weights of chlorine and the oxide of chlorine. What can you say from these data regarding the number of atoms in the chlorine molecule?

28. Calculate the number of grams of hydrogen in a vessel of 500 ml capacity when hydrogen is forced in at 100 atm at 200° using (a) simple gas laws, (b) Berthelot equation, (c) Hougen–Watson chart.

29. At what temperature will the velocity of carbon dioxide equal the velocity of oxygen at 0°? What is this velocity?

30. It takes 30 minutes for the pressure of a certain evacuated vessel of 1-liter capacity to rise from 0.001 mm to 0.003 mm by leakage of air through a pinhole in the glass. How long will it take for chlorine at the same temperature and external pressure to leak in and raise the pressure from 0.001 mm to 0.003 mm? The average molecular weight of air is 28.8.

31. Calculate the volume of 100 g of methane at 0° and 100 atm using (a) ideal-gas laws, (b) van der Waals' equation, (c) Berthelot's equation, (d) Hougen–Watson chart.

32. (a) Using the Hougen–Watson chart, estimate the volume of a vessel necessary to hold 1000 g of octane, n-C_8H_{18} at 354° under a pressure of 50 atm.

(b) How is this chart to be interpreted if 1000 g of octane is placed in this vessel under 50 atm pressure at 183°?

33. A glass bulb fitted with a stopcock was evacuated and found to weigh 46.8542 g without correcting for the buoyancy of the air. When the stopcock was opened and dry air was allowed to fill the bulb, the weight increased to 47.0465 g. The barometric pressure was 745 mm of Hg, and the temperature was 27°.

(a) Calculate the total volume of the bulb from the known molecular weight of air, 28.8.

(b) Calculate the weight if the bulb were filled with dry hydrogen at this temperature and pressure.

34. A temperature scale using an ideal-gas thermometer is defined by taking the melting point of mercury as zero and its normal boiling point as 100°. Calculate the normal boiling point of water and the absolute zero on this scale. Mercury boils at 356.9° and freezes at −38.87°.

35. Using the data of Problem 17, determine the limiting value of d/p at zero pressure and the atomic weight of nitrogen, not by graphing, but by calculation, using the method of least squares.

36. Calculate the pressure necessary to compress 1 mole of CO_2 to a volume of 0.200 liter at a temperature of 50° using (*a*) the gas law: $pv = nRT$; (*b*) the Beattie–Bridgman equation (appendix, page 673). The constants for CO_2 are as follows when p is expressed in atmospheres, V in liters per mole, and T in degrees Kelvin: $A_0 = 5.0065$; $a = 0.07132$; $B_0 = 0.10476$; $b = 0.07235$; $c = 6.600 \times 10^5$.

37. Ordinary carbon contains 98.9 per cent of carbon with a mass of 12.00 and 1.1 per cent of an isotope of carbon with a mass of 13.00. By a certain physical-chemical operation (page 636) the concentration of this isotope is increased from 1.1 to approximately 2.0 per cent. It is planned to determine the exact percentage of this heavier isotope by measuring the density of carbon dioxide with a gas-density balance. If this concentration of 2 per cent must be known to one part in 500 for the experiment planned, how accurately in parts per million must the gas density of the CO_2 be measured? To what fraction of a degree must the temperature be known at about 25° and to what fraction of a millimeter must the pressure be known at about 740 mm in order to achieve this accuracy?

CHAPTER III

ATOMIC AND MOLECULAR FORCES

In the preceding discussion of gases, it became clear that the attraction between atoms and molecules varies considerably, and it was evident that information regarding these forces would be helpful in making physical-chemical predictions. In the present chapter some of the underlying principles of atomic and molecular structure are presented so that they may find applications in the subsequent study of physical-chemical phenomena.

All matter is composed of chemical compounds or mixtures of chemical compounds which in turn are composed of 96 different kinds of elements. The units of these elements are the atoms, each atom weighing $1/6.02 \times 10^{23}$ of the atomic weight. These atoms possess a complicated structure consisting of an extremely dense positively charged nucleus surrounded by light negative electrons in definite energy levels. The nucleus also is complex and is made up of protons, which are the nuclei of hydrogen atoms, and neutrons which have nearly the same weight as the protons but possess no electric charge. The number of protons in the nucleus determines the positive charge on the nucleus, and this, in turn, is equal to the number of extranuclear electrons in the atom. This number is defined as the *atomic number*. The theories and the experimental foundation for the structure of the atom and the nucleus are given in Chapter XXI.

The Periodic Table. Hydrogen is the lightest atom with a nuclear charge of one and one extranuclear electron, and uranium is the heaviest naturally occurring element with an atomic number of 92. The heaviest atom is curium with 96 positive charges on the nucleus surrounded by 96 electrons. All the other elements have atomic numbers between one and 96. These electrons are arranged in shells around the central nucleus of the atom, the number in each shell being limited by the rules of the quantum theory, discussed on page 576.

The maximum number of electrons in the first shell is two; the maximum in the second shell is eight; and larger encircling shells are limited to 18 and 32. Attempts have been made to visualize these shells of electrons as cubes with eight corners, or as a series of elliptical orbits in which the electrons travel. However, these pictures are incomplete and

unnecessary. The limitations of the number of electrons in a given shell lead to the familiar periodic table of the elements given on page 665, where the atomic numbers are shown. The atomic number of an element determines its position in the periodic table, and its chemical properties.

Hydrogen has one extranuclear electron, and helium has two. The first group can include only two electrons, and so lithium with three electrons has to start a new shell with its extra electron. Beryllium with an atomic number of 4 has four electrons, two of which are used in filling the first shell and two of which go into the second shell. Boron has three in the second shell; and carbon four, etc.

Neon with an atomic number 10 has the two positions in the first shell and all eight positions in the second shell occupied. Its outermost shell is complete; and the next element, sodium, with an atomic number 11, has to start a third shell with one electron. Magnesium with an atomic number 12 has two electrons in the first shell, eight electrons in the second, and two in the third shell. In similar manner, as the elements increase in atomic number, the electrons fill up the shells and then start to fill the shells farther removed from the nuclei.

The number of electrons which can be readily moved determines the valence and many chemical properties. The alkali metals, lithium, sodium, and potassium, are alike in having one electron in the outermost shell which can be easily removed, and they are similar in their chemical properties. Beryllium, magnesium, and calcium each have two electrons in the outermost shell, whereas fluorine and chlorine each have seven electrons in the outermost shell. The grouping of like elements in the periodic table is thus traced to the similarity in electron arrangement. The rare gases with completed shells are stable. Elements with only one electron in the outermost shell may lose that electron and tend to simulate the rare gas of next lower atomic number, whereas elements with nearly complete rare-gas configurations tend to attach more electrons and simulate the rare gas next higher in atomic number. The former elements have metallic properties, whereas the latter elements have nonmetallic properties. In sodium, where there is no tendency for the atoms to gain electrons, electric conductance is good; but in sulfur, where an atom may tend to complete its quota of eight electrons by attaching two more to complete its shell, electrons cannot migrate and the electric conductance is very slight.

In the larger shells with 18 or 32 electrons there may be several different possible electronic arrangements of nearly equal energy; hence, the positive valence is variable. Moreover, the ions may be colored when the possible electron displacements involve energy differences so small that they correspond to the energy of visible light.

Electron Theory of Valence. The combination of atoms to give a variety of molecules is of fundamental importance in all chemical reactions and biological processes. In later chapters the laws which govern chemical equilibrium and reaction rates are studied, and it will be seen that the course of a chemical reaction can be predicted with fair accuracy when a sufficient number of factors are known.

A simpler method of presenting the facts of chemical combination is desirable. It is necessary for the chemist to know which combination of atoms are stable and which are not. The permissible ways in which atoms can go together to form compounds have been handled in a very satisfactory manner by the rules of valence in which carbon is given a combining power or valence of 4, hydrogen of 1, oxygen of 2, and so on. Much of the success of chemistry and particularly organic chemistry has been due to this simple concept.

However, these valence rules are unsatisfyingly empirical and often inadequate. Attempts have been made to put the concept of valence on a more fundamental basis and to make it more widely useful. The theories of the electron pair and the octet and mathematical approaches based on the quantum theory (which are discussed in Chapter XIX on page 576) have been the result. The more general and accurate theories are complicated, and one must choose between simplicity and accuracy. For many purposes the older idea of valence hooks is sufficient, but the electron pair and, to a limited extent, the octet are useful, particularly in organic chemistry.*

The forces that hold atoms together in organic molecules and in substances like nitrogen and hydrogen differ from those which are found in inorganic compounds and in electrolytic solutions. The distinctions between these two different types, the *nonpolar* and the *polar* compounds, will be stressed many times. The polar compounds involve chiefly electrostatic forces, giving rise to *heteropolar bonds* or ionic linkages. The nonpolar or *homopolar bonds* or *electron-pair bonds* involve an "exchange energy" understandable on the basis of quantum mechanics. It is not to be thought, however, that atoms are held together exclusively by one type of bond or the other. In most linkages between atoms both electrostatic attraction and exchange energy binding are operating. There are all gradations between linkages that are predominantly homopolar and those that are predominantly heteropolar, so that complete quantitative treatment is not yet possible.

These two different types of binding were correlated and the concept

* Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939; Johnson, in Gilman's "Organic Chemistry," John Wiley & Sons, New York, 1940, Chapter 19.

of valence was amplified by the hypothesis of the electron pair proposed by G. N. Lewis in 1916. According to this hypothesis there is a definite tendency for electrons within a molecule to go together in pairs. The hypothesis is in agreement with the quantum theory.

The tendency of electrons to go in pairs is almost universal, so universal, in fact, that only a few molecules containing an odd number of valence electrons are known. When these odd molecules do exist, they are abnormal. They tend to associate, and they are usually colored. Nitrogen dioxide and triphenylmethyl are examples.

In the hydrogen molecule 14 per cent of the attraction is due to electrostatic forces and 86 per cent to homopolar or electron-pair binding, but in most molecules the relative importance of the two types of attraction is not known quantitatively. The presence of these two types of binding in unknown ratios is a serious handicap in the quantitative application of these concepts.

Another rule for the arrangement of electrons within a molecule, the octet hypothesis, has been proposed by Lewis,* by Kossel, and by Langmuir. According to it, there is a tendency for eight electrons to group around each atom in a molecule. There are exceptions, and they make this rule less significant than the rule of the electron pair.

These hypotheses may be illustrated with lithium fluoride. Lithium has one electron in its outermost shell, and fluorine has seven. The lithium atom tends to lose its one valence electron in the outermost shell, becoming a lithium ion with one positive charge, and the fluorine atom tends to gain an extra electron, becoming a fluoride ion with one negative charge. Both tendencies are satisfied by a transfer of an electron from the lithium to the fluorine. This electrostatic or ionic type of linkage can be broken apart by dissolving the compound in certain solvents. Lithium fluoride, for example, separates almost completely into lithium ions and fluoride ions when dissolved in water. The energy required to pull these ions apart is partially offset by the energy released when the ions combine with the solvent.

Other examples are given by the following equations, in which the numbers of electrons in the outermost shell are indicated with dots. Thus:

$$\mathrm{Li}\cdot + \cdot\ddot{\mathrm{F}}\!: = \mathrm{Li}\!:\ddot{\mathrm{F}}\!: = [\mathrm{Li}]^+ + [\mathrm{F}]^-$$

$$\mathrm{H}\cdot + \cdot\ddot{\mathrm{Cl}}\!: = \mathrm{H}\!:\ddot{\mathrm{Cl}}\!: = [\mathrm{H}]^+ + [\mathrm{Cl}]^-$$

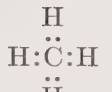
$$\mathrm{Li}\cdot + \cdot\mathrm{H} = \mathrm{Li}\!:\!\mathrm{H} = [\mathrm{Li}]^+ + [\mathrm{H}]^-$$

* Lewis, *J. Chem. Phys.*, **1**, 17 (1933); "Valence and the Structure of the Atom," Chemical Catalog Co., New York, 1923.

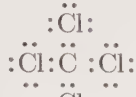
A covalent bond or homopolar bond, represented with two dots for the electron pair, is the same as the valence bond of organic chemistry. The following equations and formulas illustrate the *covalent bond:*

$$H\cdot + \cdot H = H:H$$

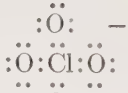
$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: = :\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{Cl}}:$$



Methane



Carbon tetrachloride



Perchlorate ion

It is interesting to note that these views of valence account satisfactorily for the fact that a hydrogen atom will combine with an atom of negative chlorine, with an atom of positive lithium, or with another atom of hydrogen.

Double bonds and triple bonds can be represented by the sharing of two pairs or three pairs of electrons, as shown by ethylene and acetylene.

Ethylene

$$H:C:::C:H$$

Acetylene

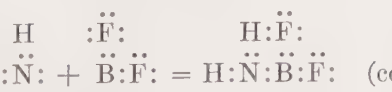
In an elaborated electron theory not only the positions of the electric charges or polarization are important but also their mobility or polarizability. Both these quantities can be given roughly in terms of values assigned to pairs of atoms and atomic groups; but the influence of structure and of solvents affects the behavior also.

There is a special type of covalent bond, called a *coordinate covalent* bond, in which both electrons of the electron pair are contributed by the same atom, thus:

$$x\cdot + \cdot y = x:y \quad \text{(normal covalency)}$$

$$x: + \ y = x:y \quad \text{(coordinate covalency)}$$

This type of linkage is recognized among organic and inorganic molecules as giving rise to special properties. An example is given among the boron compounds



(coordinate covalency)

The concept of resonance is useful, and it can be measured quantitatively. *Resonance* exists when nuclei are arranged in a molecule in such a way that, by the rapid shifting of electrons from one position to another, two or more different structures can exist in which the energies are nearly the same. Thus there are several different ways in which the benzene ring can be drawn. For example, it may have different arrangements of alternating single and double bonds, or it may perhaps be drawn with six single bonds in the ring and the other valence bonds stretching directly across the center of the ring. Other structures are also possible.

By rapidly oscillating between the various positions, the electrons can give to benzene some of the properties expected from each of these structures. When such a situation exists, the energy of formation is increased, more energy is required for decomposition, and the molecules possessing resonance have an increased stability. This fact explains why benzene and the aromatic compounds, in general, are so stable.

The existence of resonance and the extent of the resonance energy may be determined by comparing the abnormally low heat of reaction with the normal value calculated from the sum of the parts of the molecule. Another test for resonance is obtained by comparing the distance between atoms in the molecule with the normal interatomic distance of the bond as obtained from electron diffraction patterns (page 85). If there is resonance in a molecule, the distance between atoms in the resonance structure will be less than the normal distance found in other molecules. Molecules containing conjugated double bonds, that is, (—C=C—C=C—), are particularly favorable for the rapid movement of electrons and the formation of a molecule with resonance.

Another concept in the electron theory of valence is that of the *hydrogen bond,** which in special cases attracts two atoms so strongly that it appears to act as a bond between them. The hydrogen atom is unique, owing to the fact that, when its electron becomes detached, only the nucleus of very small diameter is left. In no other element can the atoms acquire nuclear dimensions by the loss of a single electron. The hydrogen nucleus is so small that apparently it can attract two strongly negative atoms.

The formation of HF_2^- ion, the formation of double molecules of organic acids, and abnormal behavior in some liquids and solutions can be explained on the basis of hydrogen bonds.

Electrostatic Attractions. As already stated, electrostatic attraction is important in holding atoms together in crystals, molecules, and

* Lassettre, *Chem. Rev.*, **20**, 259 (1937); Rodebush, *Chem. Rev.*, **19**, 59 (1936); Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca N. Y., 1940.

loose intermolecular complexes. Even in essentially homopolar bonds some of the force holding the atoms together is electrostatic in nature. Electrostatic attraction applies not only to ions but also to dipoles and induced dipoles. An ion is an atom or group of atoms with a definite electric charge caused by the addition or removal of electrons. A dipole is a molecule in which the positive and negative charges are equal but arranged in such a way that part of the molecule is predominantly positive and another part predominantly negative so as to give an electrical unbalance. The magnitude of the total effect in the molecule is measured quantitatively by the dipole moment (page 86). Water is a good example of a substance which has a large dipole moment. Induced dipoles are produced by the proximity of a charged part of a neighboring molecule. They are present in most substances, but they show up more prominently in a substance like helium where the other forces are absent. Although helium has no charge and no dipole moment, it still contains a positive nucleus and a negative electron which induces a charge in a neighboring molecule. This attraction of the induced dipoles is very small in helium but is responsible for its liquefaction at very low temperature.

There are six different combinations of these three different types of electrostatic binding. Examples are known of each type. It must be realized that there is no sharp distinction between types and that frequently several of these interactions are involved simultaneously.

Ion–Ion. The attraction between sodium and chloride ions is an example of this ionic type of binding. Ionic bindings are much stronger than most homopolar bonds. The separation of the nuclei plays an important part. Thus, a hydrogen ion or a sodium ion is held much more tightly to a fluorine ion than to an iodide ion.

Dipole–Dipole. When two unit dipoles are aligned head-on, thus $(-+)(-+)$, considerable energy is required to pull them apart to infinite distance. When they are surrounded by a liquid of high dielectric constant, the energy required is considerably less. This dipole attraction leads to association of liquids such as water and the alcohols and polar substances. The association involves an indefinitely large number of units and is different in character from double molecules such as are formed in the association of the organic acids. Substances which have very low dipole moments can, nevertheless, possess an appreciable attraction. Thus, although carbon tetrachloride has a dipole moment of zero, this refers to the net moment of the whole molecule; there are positive and negative parts of the C—Cl bond, that is, bond moments, which result in the mutual attraction of C—Cl bonds on adjacent molecules.

Many of the loose chemical compounds found in mixtures of liquids are held together by this dipole interaction.

Induced Dipole–Induced Dipole. Although quite general, this type of attraction is frequently so small in comparison with the other types of attractions that it is unnoticed. It is the small attractive force which is responsible for the liquefaction of helium at very low temperature.

Ion–Dipole. This type of attraction is very important because it is responsible for the solubility of electrolytes in water.

Ion–Induced Dipole. Certain complex ions are produced by the attractive force existing between an ion and a dipole induced in a neighboring molecule. In the reaction,

$$I^- + I_2 = I_3^-$$

part, at least, of the energy of combination is due to this ion–induced-dipole attraction.

Dipole–Induced Dipole. The solubility of helium and the rare gases in water is due to this type of attraction. If there were no attraction between helium and water there would be no reason to expect solubility. In fact, there is evidence for the formation of an argon hydrate; and a crystalline hydrate of butane is known.

It is possible to treat these electric attractive forces semiquantitatively * as well as qualitatively, using simple formulas which involve distance apart of the two attracting units, dielectric constant of the solvent, and other factors.

REFERENCES

Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

Johnson in Gilman's "Organic Chemistry," John Wiley & Sons, New York, 1943, Chapter 19.

Rice, "Electronic Structure and Chemical Bonding," McGraw-Hill Book Co., New York, 1940.

Sidgwick, "The Electron Theory of Valence," Oxford University Press, 1929.

Lewis, "Valence and the Structure of the Atom," Chemical Catalog Co., New York, 1924; *J. Chem. Phys.* **1,** 17 (1933).

Van Vleck and Sherman, *Rev. Mod. Phys.*, **7,** 176 (1935).

Remick, "Electron Interpretation of Organic Chemistry," John Wiley & Sons, New York, 1943.

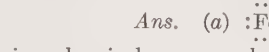
* Moelwyn-Hughes and Sherman, *J. Chem. Soc.*, 101 (1936); Moelwyn-Hughes, "Physical Chemistry," Cambridge University Press, Cambridge, 1940, pages 92–103.

PROBLEMS

1. Write the following structures in terms of the electron theory of valence: (*a*) Perchlorate ion ClO_4^-; (*b*) sulfate ion SO_4^{--}; (*c*) phosphate ion PO_4^{---}; (*d*) cupric ammonium ion $Cu^{++} \cdot 4NH_3$.

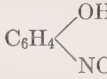
Ans. (*a*)

2. Write the following reaction in terms of the electron theory of valence: (*a*) $Fe^{++} \rightarrow Fe^{+++} +$ electron; (*b*) $Zn + S \rightarrow ZnS$; (*c*) $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$; (*d*) $C_2H_6 + 2Cl_2 \rightarrow C_2H_4Cl_2 + 2HCl$.

Ans. (*a*) 

3. Represent the following chemical compounds on the basis of the electron theory of valence: (*a*) H_2; (*b*) LiH; (*c*) CH_4; (*d*) HCl; (*e*) Cl_2.

4. Sodium dichloroacetate, $CHCl_2COONa$, dissociates into dichloracetate ion and sodium ion when dissolved in water. Write the structure for this compound on the basis of the electron theory of valence, and state which bonds are homopolar bonds and which are heteropolar.

5. Indicate with sketches how a hydrogen bond might be formed in (*a*) ethanol C_2H_5OH, (*b*) acetic acid CH_3COOH, (*c*) nitrophenol  .

6. Draw several benzene rings containing six carbon atoms each with four valencies, two of which hold the ring together and the third of which is attached to a hydrogen atom. Each carbon atom has one valence left over, and these may form double bonds among any three pairs of atoms. Show that there are six different ways in which the three extra bonds can be drawn, including alternating double bonds. The presence of these several different possible structures results in resonance and gives to benzene its stability.

7. Give illustrations of the interactions involving ions, dipoles, and induced dipoles.

CHAPTER IV

THE CRYSTALLINE STATE

Properties of Solids. In solids there are strong forces which hold together the atoms and molecules, thereby giving the solids fixed shape, rigidity, and mechanical strength. These forces are of several different kinds which produce a wide difference in the physical properties of the solids, as observed, for example, in crystalline solids and amorphous solids.

Amorphous solids such as pitch or glass may be regarded as supercooled liquids in which the force of attraction holding the molecules together is so great that the material is rigid. *Crystalline* solids are those in which the atoms are arranged in some definite order constantly repeated. The binding force in this case may be due to an electric attraction between positive and negative ions in the crystal as in the case of sodium chloride; to the existence of chemical bonds in which the atoms are held together by valence bonds in continuing structures, as in the case of diamond; or to attraction between molecules arranged in definite order, as in the case of solid carbon dioxide.

The crystalline and the amorphous solids differ in several respects. A pure crystalline material usually has a sharp melting point. It remains solid up to a definite temperature and then melts to the liquid state at a temperature only slightly higher. When an amorphous solid is heated, it gradually softens and becomes mobile over a wide range of temperature without undergoing a sharp change from solid to liquid. The surfaces of an amorphous substance do not, in general, exhibit definite recurring faces at definite angles, such as are often displayed by crystalline solids. The regular internal arrangement of the units of a crystalline solid lead to the formation of definite patterns when X rays are passed through them, as will be explained shortly. Although amorphous solids also give rise to the diffraction of X rays, the phenomenon is much less pronounced.

The properties of a crystal such as tensile strength, elasticity, heat conductance, electric conductance, rate of transmission of light, and rate of solution may be different along the different axes of the crystal; and such a crystal is called *anisotropic*. An *isotropic* crystal is one which has the same properties in all directions. The characteristic

color patterns of anisotropic crystals with polarized light (discussed on page 71) are used for identification, particularly in the microscopic examination of chemicals and minerals.

Use can be made of the fact that the rate of solution of an anisotropic crystal is greater in one direction than in another. The surface is etched by the addition of nitric acid or picric acid or other chemical solvent in such a way as to bring out characteristic patterns. In solids which are mixtures of different chemical substances etch figures are brought out by chemical reagents which attack the materials at different rates and give valuable information concerning the heat treatment and previous history of a metal. It is usually desirable to grind and polish the metal to give a very smooth surface before examining it with a microscope. This technique has been helpful in proving with photomicrographs that a piece of metal came from a particular source. That strains set up in a solid can lead to different behavior is shown by the fact that numbers stamped in a piece of metal and filed smooth can often be reconstructed by a careful etching process.

Different chemical substances often have crystal forms which are very much alike. If they have the same crystal form and nearly identical angles, they are said to be *isomorphous*. Usually they are similar in chemical composition, as, for example, the various alums such as $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$, $Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$, or $Cr_2(SO_4)_3 \cdot Na_2SO_4 \cdot 24H_2O$. One of the best tests for isomorphism consists in placing a crystal of one substance in a supersaturated solution of the other. If the crystal continues to grow in the same form, the two substances are isomorphous. Unless the form and crystal angles are very closely the same, the crystal will not continue to grow in perfect shape in the solution of the new substance.

The size and perfection of crystals depends to a large extent on the rate at which they are formed. The slower the rate of crystallization, the more perfect is the crystal, because the atoms or molecules have more time to find their proper positions in the crystal lattice. Great progress has been made during the past few years in growing large and perfect crystals. The purified salt is melted in a large pot which is then allowed to cool very slowly at a definite automatically controlled rate. In this way sodium chloride, silver chloride, potassium bromide, lithium fluoride, and other salts have been prepared in large transparent pieces several inches in diameter which are valuable for optical work.

Crystal Forms. Chemical compounds exist in a great many different crystal forms, depending on the type of binding force, the kind of atomic grouping, the relative size of the different ions or atoms, and many other factors. Many thousand different crystals are known, distinguishable

one from another by shapes, angles between faces, and X-ray diffraction patterns. In spite of the great variety of crystal forms, a given chemical compound or mineral will always exhibit the same angle between two given faces at a given temperature. This law was discovered first by Steno in 1669. It provides an excellent means for the identification of materials by the determination of the crystalline

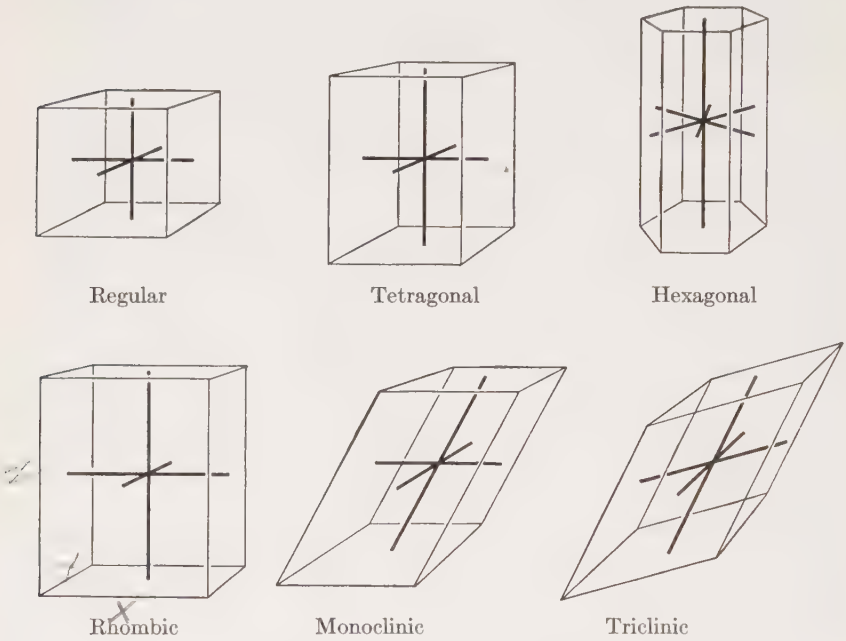


Fig. 10. The six crystal systems.

properties. Large crystals may be measured directly; small crystals obtained by evaporating a solution may be examined with a microscope; and all crystals may be studied by measuring the diffraction of X rays when passed through crystals or reflected from them.

The large number of different crystals may be reduced to several general types which, in turn, can be referred to three or four axes and classified into six different fundamental systems, as shown in **Fig. 10** and described in the following paragraphs:

In the *regular* or cubic system there are three axes of equal length intersecting at right angles in space.

The *tetragonal* system also contains three axes intersecting at right angles, but two are equal in length, and the third is either longer or shorter.

In the *hexagonal* system there are three axes of unit length, all in the same plane and intersecting at angles of 60°, and a fourth axis, either longer or shorter and perpendicular to the plane of the other three.

In the *rhombic* system the three axes of unequal length all intersect each other at right angles.

In the *monoclinic* system there are three axes of unequal length, two of which intersect at right angles, while the third axis is perpendicular to one and not to the other.

In the *triclinic* system there are three axes of unequal length, no two of which intersect at right angles.

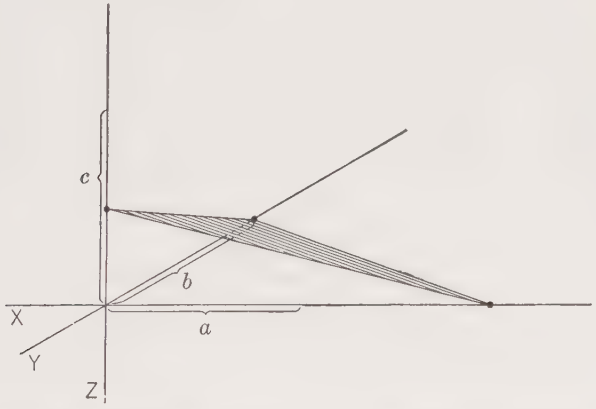


FIG. 11. Intersection of a plane on the crystal axes indicating the calculation of Miller indices.

A crystal face may be described in terms of an angle which it makes with a reference plane, or it can be described more usefully for theoretical studies by giving its intercepts on the three standard axes, X, Y, and Z. In the simplest systems the X and Y axes make right angles with each other in a horizontal plane as in any system of rectangular coordinates. The third axis Z is vertical, being perpendicular to both X and Y and passing through their intersection. The system commonly used for defining crystal faces in terms of their intercepts on the X, Y, and Z axes was proposed by Miller in 1829. Unit distances along these axes are called a, b, and c, respectively, and *Miller indices* are described as the reciprocals of the intercepts on the axes in terms of these unit distances.

The application of the Miller indices to a rhombic crystal in which all the axes are at right angles is indicated in **Fig. 11** which shows the crystal axes, X, Y, and Z, with a plane cutting the X axis at $2a$, the Y axis at b, and the Z axis at $\frac{1}{2}c$. The intercepts are 2, 1, and $\frac{1}{2}$; their reciprocals are $\frac{1}{2}$, 1, and 2; and the Miller indices are written 1, 2, 4.

The reciprocals of the intercepts are multiplied by an appropriate number so that no fractional numbers remain, the relative values of the intercepts being unaffected by the multiplication. The faces of crystals are usually of such a nature that the indices are small numbers: 1, 2, 3, 4, etc.; or, if they are parallel to the axis, they cut it at ∞ and the Miller index is zero.

In case the X, Y, and Z axes do not intersect at right angles, it is necessary to specify the angles as well as the intercepts.

X Rays and Crystal Structure. Important information concerning the arrangement of the atoms and molecules within crystals has been

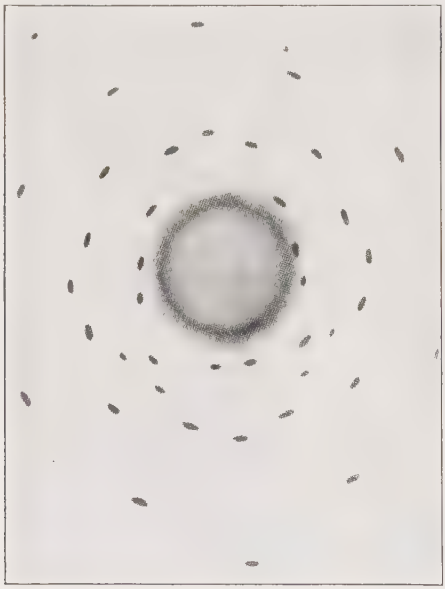


FIG. 12. Laue X-ray diffraction pattern.

obtained from the measurements of the transmission and reflection of X rays. X rays are radiations having wave lengths of the same order of magnitude as the distance between atoms in crystals, and, accordingly, it is possible to obtain interference of X rays in crystals. Following a prediction of Laue in 1912 that the regularly arranged atoms of a crystal should act as a three-dimensional diffraction grating, Friedrich and Knipping passed small beams of X rays through crystals and obtained on a photographic plate a large number of points arranged in a symmetrical pattern around the central point, which was caused by the undeviated beam. An X-ray picture of magnesium oxide is given in **Fig. 12.**

Patterns such as this can be interpreted by building up, mathematically, crystal models in space. The distance between the atoms is adjusted arbitrarily along the different axes until it is possible to obtain a calculated pattern of interference which is identical with that obtained on the photographic plate.

The reflection or Bragg method of X-ray analysis gives results that are easier to interpret than the Laue transmission method, because in the Bragg method the crystal can be regarded simply as a series of atomic planes spaced at definite intervals, extending inward from the surface and acting as interference planes in much the same way that a stack of thick glass plates would reflect a beam of visible light. Such a bundle of plates will reflect incident light only at certain definite angles, which depend both on the thickness of the plates and the wave length of the light.

A simple relation exists between the wave length of the X rays, the distance between atomic planes in the crystal, and the angle of reflection.

Figure 13 gives the cross section of a crystal in which the horizontal lines represent a series of identical planes of atoms or ions, each separated by the distance d. The plane ABC is drawn perpendicular to the incident beam of parallel monochromatic X rays, and the plane

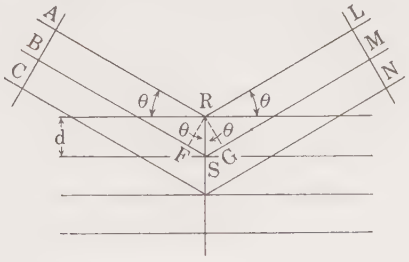


FIG. 13. Diagram used in proving that $n\lambda = 2d \sin \theta$.

LMN is drawn perpendicular to the reflected ray. The incident beam is arranged to hit the surface of the crystal at such an angle θ that all the light is in phase at the two planes ABC and LMN, that is, the distance between the two along a ray is a whole-number multiple of the wave length λ.

It can be shown that the angle of reflection is equal to the angle of incidence. The lines RF and RG are drawn perpendicular to the beams, and it can be seen that the ray BSM travels farther than the ray ARL by an amount equal to $FS + SG$. This extra distance is equal to a whole number n of wave lengths because the angle θ is such that the light at LM is in phase with the light at AB.

Then,

$$FS + SG = n\lambda \tag{1}$$

Furthermore, since

$$\sin\theta = \frac{FS}{d} = \frac{SG}{d}$$

$$FS = SG = d\sin\theta$$

and

$$n\lambda = 2d\sin\theta \tag{2}$$

This is an important equation which gives the relationship of the distance between atomic or ionic planes in a crystal and the angle at which the reflected radiation has a maximum intensity. Similar calculations can be made for the reflection from other crystal planes lying deeper in the crystal lattice. If the rays strike the crystal at angles other than θ, the extra distance $FS + SG$ will be such as to give fractional parts of a wave length, and there will be interference of the light reflected from the different crystal planes, which will result in a weakening of the intensity of the reflected light.

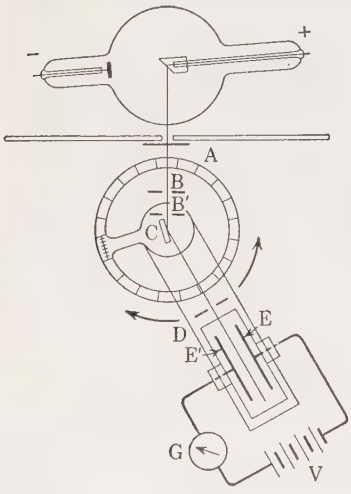


Fig. 14. X-ray spectrometer.

The reflection corresponding to $n = 1$ is called the first-order reflection, the reflection corresponding to $n = 2$ is the second-order reflection, and so on. Each successive order exhibits a wider angle and weaker intensity.

The maxima are found by rotating the crystal so as to change the angle θ at which the X-ray beam strikes the surface. If the X rays are incident on the face of a crystal for which d is known, the value of λ for the radiation used may be determined by measuring the angles at which the reflections of maximum intensity occur. On the other hand, if the wave length of the incident radiation is known, it becomes possible to determine the spacing of the atomic planes of atoms or ions within the crystal.

The intensity of reflection of X rays at various angles can be determined by the blackening of a photographic plate, or, more accurately, with an X-ray spectrometer using an ionization chamber as shown in **Fig. 14.** In this instrument a beam of X rays, generated as described

on page 621, passes through a filter at A and is rendered parallel by means of two narrow slits B and B'. After passing through these slits, the rays are reflected from one of the faces of a crystal C, which is mounted as a reflection grating on the table of the spectrometer; and the reflected beam then passes through a slit D and enters an ionization chamber where its intensity is measured.

The ionization chamber contains two electrodes, E, E', connected to a high-voltage battery V through an electrometer G, the space between the electrodes being filled with sulfur dioxide or other gas which is easily ionized by X rays.

In the absence of X rays or other ionizing rays, the gas between the electrodes acts as an insulator, and no current flows through the electrometer; but, when X rays pass through the gas, they form ions which are drawn to the electrodes, thus producing a current. The magnitude of the electrometer deflection depends on the number of ions formed which, in turn, is a measure of the intensity of the X rays. The crystal at the center and the ionization chamber attached to it are rotated around the spectrometer table and the electrometer deflections are recorded at each setting of the table. The deflections are then plotted against the angle of rotation to obtain the angles at which maximum reflection occurs as shown later in Fig. 18.

Cubic Lattices. The *regular* system is the simplest of the crystal systems, and so it is explored here in some detail. From a visual examination of sodium chloride it is evident that sodium chloride belongs to the cubic or regular system, with three equal axes all at right angles, but there is a possibility of three different cubic lattices as shown in the following figures. The *simple cubic*, shown in **Fig. 15,** has eight struc-

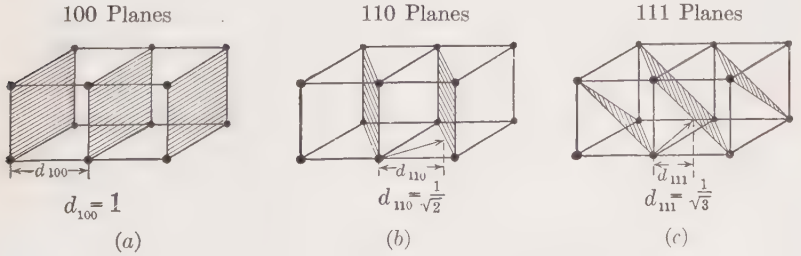


FIG. 15. Simple cubic lattice.

tural units, represented by black dots, one at each of the corners of a cube. These structural units might be charged ions, atoms, or molecules, and the arguments for deciding that they are ions in the case of sodium chloride will be presented a little later. The face-centered cubic lattice

shown in **Fig. 16** has 14 ions, one at each of the eight corners and one at the center of each of the six faces.

The body-centered cubic lattice shown in **Fig. 17** has nine ions, one at each of the eight corners and one in the center.

Through the use of X rays it is possible to establish the distances between the different sets of planes in a given cubic crystal and to determine to which of the three types the crystal belongs.

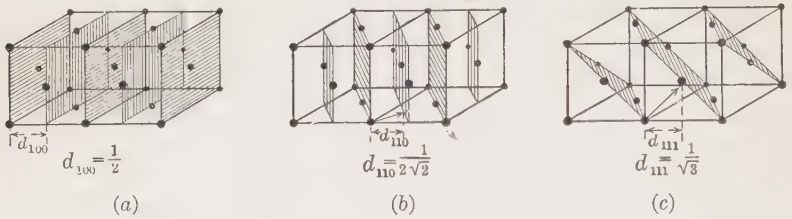


FIG. 16. Face-centered cubic lattice.

In the simple cubic lattice shown in Fig. 15*a*, the (100) planes cut the X axis and are parallel to the Y and Z axes. In Fig. 15*b*, the (110) planes cut obliquely across the X and Y axes but cut the Z axis at infinity, that is, they are parallel to the Z axis. The Miller indices for such a plane are (110), as already explained. In Fig. 15*c*, the planes cut obliquely across all three axes, intercepting each at the same distance from the origin and giving the Miller indices (111). The distance between (100) planes, d_{100}, is obviously the length of a face or 1. The

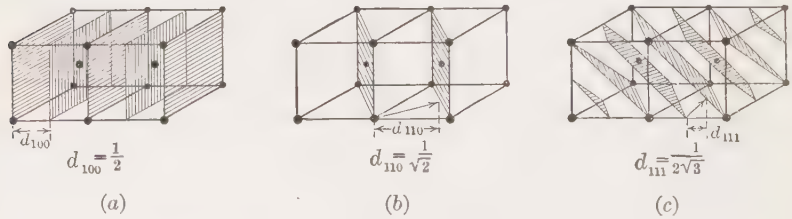


FIG. 17. Body-centered cubic lattice.

perpendicular distance between the (110) planes, d_{110}, is half the diagonal of a face, $\sqrt{2}/2$ or $1/\sqrt{2}$. The perpendicular distance between the (111) planes, d_{111}, is $1/\sqrt{3}$, a fact which is demonstrated geometrically on page 673 of the appendix.

In the face-centered cubic lattice additional (100) planes can be passed through the black dots representing the crystal units as shown in Fig. 16*a* by vertical shading. They pass vertically through the

center of the front and back faces, and the distance between planes, d_{100}, is now $\frac{1}{2}$ on the assumption that d_{100} for the simple lattice is 1.

An additional set of (110) planes parallel to the first set can be passed through the face-centered cubic lattice, as shown in Fig. 16*b*. These additional planes with vertical shading include the units in the centers of the front and side faces and come midway between the planes of the simple cubic lattice. The distance between planes then is one half as great as it is in the simple cubic lattice, and d_{110} is $\frac{1}{2} \times 1/\sqrt{2}$. The (111) planes of the simple lattice already pass through the centers of all the faces of the face-centered lattice, as shown in Fig. 16*c*, and no new planes can be introduced. The distance between planes, d_{111}, is then the same as in the simple lattice, namely, $1/\sqrt{3}$.

In the body-centered cubic lattice additional (100) planes parallel to the first planes can be passed through the units in the centers of the cube, as indicated with vertical shading in Fig. 17*a*. These new planes are halfway between the planes of the simple lattice, and $d_{100} = \frac{1}{2}$. The (110) planes, as shown in Fig. 17*b*, already pass through the unit in the center of the cube, so that no new planes are possible. The value of d_{110} is then the same as it was in the simple cubic lattice, namely, $1/\sqrt{2}$. The (111) planes, as shown in Fig. 17*c*, do not pass through the central units; and it is possible to insert another set of parallel planes through these units midway between the (111) planes of the simple lattice, as indicated with opposite shading. The distance between planes then is half as great, and $d_{111} = \frac{1}{2} \times 1/\sqrt{3}$.

The ratios of the distances between the three different sets of planes in the three different types of cubes can now be summarized.

Simple cubic lattice:

$$d_{100}:d_{110}:d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1:0.707:0.577 \tag{3}$$

Face-centered cubic lattice:

$$d_{100}:d_{110}:d_{111} = \frac{1}{2} : \frac{1}{2\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1:0.707:1.155 \tag{4}$$

Body-centered cubic lattice:

$$d_{100}:d_{110}:d_{111} = \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} = 1 : \frac{2}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1:1.414:0.577 \tag{5}$$

It will now be shown how X rays can be used to determine which of these possible structures a crystal actually has.

Crystal Lattice of Sodium Chloride as Determined with X Rays. The angles through which X rays are reflected from sodium chloride with maximum intensity are shown in **Fig. 18.** These measurements were obtained with a spectrometer such as that shown in Fig. 14, using a palladium target in an X-ray tube which gives two X rays differing slightly in wave length. The X ray used in the calculations is shown in full lines, the other in dotted lines. Three different spectra are obtained by mounting the crystal in the spectrometer in different ways and arranging to have the X rays reflected from the (100) plane, the (110)

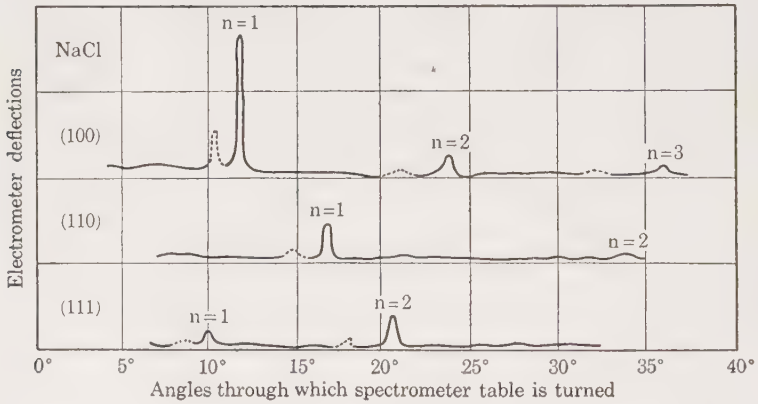


FIG. 18. X-ray reflection from sodium chloride.

or the (111) plane. The ordinates give the intensities of ionization as measured by the electrometer deflections, and the abscissas give the degrees through which the ionization chamber is turned starting from a point in line with the slits. These angles must be divided by 2 to obtain the angle θ of reflection from the crystal, because the crystal face itself is inclined toward the incident light, and the angle of reflection is equal to the angle of incidence. The first-order reflections for the planes are found to occur at spectrometer readings * of 11.8°, 16.8°, and 10.4° for the (100), (110), and (111) planes, respectively, corresponding to values of θ of 5.9, 8.4, and 5.2.

Taking the ratio of the sines of these angles, we have

$$\sin 5.9° : \sin 8.4° : \sin 5.2° = 0.103 : 0.146 : 0.091 = 1 : 1.42 : 0.88$$

and, since

$$d = \frac{n\lambda}{2 \sin \theta}$$

* The dotted maxima are due to a second X-ray spectral line.

it follows that the corresponding values of d should be in the ratio of the reciprocals of these numbers; that is,

$$d_{100}:d_{110}:d_{111} = 1 : \frac{1}{1.42} : \frac{1}{0.88} = 1:0.704:1.14$$

But we have already seen that, for a face-centered cubic crystal,

$$d_{100}:d_{110}:d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1:0.707:1.155$$

Therefore, the fundamental space lattice of a crystal of sodium chloride must be face-centered because the agreement between experimental determination and theoretical calculation is so close.

In this calculation only the first-order reflections were used, where $n = 1$. Higher-order reflection maxima corresponding to values of n of 2 and 3, etc., are obtained also, and in the (100) plane in rock salt, shown in Fig. 18, there is a first-order spectrum at 11.8, a second order at 23.7, and a third order at approximately 36.3, each becoming progressively weaker.

If we take half of these angles, $\theta = 5.9°$, 11.85°, and 18.15°, and

$$\sin\theta_1:\sin\theta_2:\sin\theta_3 = 0.103:0.205:0.312$$

These numbers are very close to the theoretical ratios, 1:2:3, for the first, second, and third orders.

The ratios of the sines of the angle of maximum reflection from the different planes establishes the fact that the crystal lattice of sodium chloride is face-centered cubic, but a comparison of the intensities of the first, second, and third orders gives additional information. The structural units of the sodium chloride crystal might be sodium chloride molecules, or there might be two separate lattices of atoms penetrating each other, the one consisting of sodium atoms or ions and the other consisting of chlorine atoms or chloride ions. If the lattice were made up of sodium chloride molecules, all units of the lattice would be the same, and the intensities of the X-ray reflections would always decrease progressively from first- to second- to third-order reflection, as is the case with the (100) reflections. It may be noted, however, in Fig. 18 that for the (111) reflections the first order at 10.4° is weak, the second order at 20.8° is strong, and the third order is missing. This fact leads to the requirement of the two interpenetrating lattices shown in **Fig. 19,** and evidence will be cited presently to show that these interpenetrating lattices are composed of ions rather than atoms.

The radius of the sodium ion is 0.96 A and that of the chloride ion is 1.83 A. As a general rule, the negative ions in crystal lattices are found to be larger than the positive ions. The square connecting chloride ions is drawn in Fig. 19, showing the face-centered lattice of the chloride ions. Similar squares, each containing five chloride ions, could be drawn on any part of the faces. A similar square is drawn with dotted lines for the sodium ions, and it is evident that such squares, each containing five sodium ions, can be drawn anywhere on any of the faces showing the face-centered lattice of the sodium ion lattice. It is to be noted that these lattices overlap by half the length of the face, so as to give an interpenetrating lattice in which the corners of the sodium cube always come halfway between the corners of the chloride cube and the corners of the chloride cube come halfway between the corners of the sodium cube.

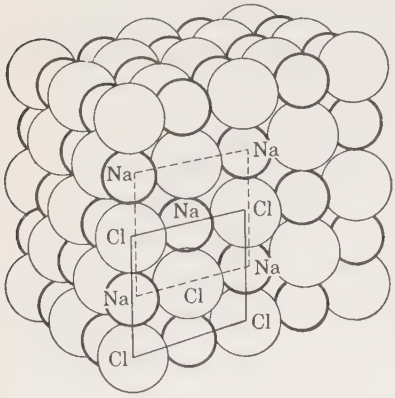


FIG. 19. Crystal lattice of sodium chloride; small spheres sodium ions; large spheres chloride ions.

A further examination of Fig. 19 shows that the (111) planes (which cut diagonally through the cubes in both horizontal and vertical planes) include only sodium ions or only chloride ions in a single plane. It may be remembered that the maximum in X-ray reflections occurs when the angle of the spectrometer is so adjusted that the paths between successive layers of ions are equal to one wave length of the reflected radiation. If the rays are reflected from the (111) planes at such an angle that the rays from successive planes of chloride ions differ in path length by a whole number of wave lengths, the rays coming from successive sodium ion planes, which are spaced equally between them, will then differ by half a wave length and cause interference. The interference would be complete except for the fact that the chloride ions are 50 per cent heavier, and, owing to the larger number of electrons in each atom, the X-ray reflections are more intense. The reflections for the first-order reflection should then be weak. For the second-order spectrum where $n = 2$, at $20.8°(\theta = 10.4)$, however there is a difference of a whole wave length between the rays from the chloride and sodium planes, so that there is no interference, and the reflection maximum is intense. The third-order spectrum again corresponds to a difference of a wave length and a half between the two sets of reflecting planes, and this interference,

combined with the fact that the third-order spectrum is naturally weaker, leads to its practical disappearance.

The fact that in the (111) reflections the second-order maximum is more intense than the first-order reflection, as shown in Fig. 18, indicates that the sodium chloride lattice is composed of two interpenetrating lattices of sodium and of chloride. The second-order reflection, however, should not be greater than the first order in the case of the (100) planes which are parallel to the sides nor in the case of the (110) planes which are vertical planes cutting the bottom plane diagonally. In these planes there are equal numbers of chloride and sodium ions, and the alternation between chloride and sodium planes found in (111) planes does not exist. Figure 18 shows that the abnormally greater intensity for the second order does not occur in the (100) and (110) planes.

This interpretation of lattices is supported by further observations on potassium chloride and potassium bromide, which also crystallize with face-centered cubic lattices. In potassium chloride the first- and third-order reflections from the (111) planes are entirely missing, as would be expected from the fact that potassium and chlorine are so nearly of the same atomic weight and number of electrons that interference is complete. Potassium bromide, however, with unlike atomic weights, gives a definite but weakened maximum for first-order reflections from the (111) plane. Its second-order reflection, of course, is more intense because there is no interference.

In the sodium chloride lattice each sodium ion is surrounded by six chloride ions and each chloride ion by six sodium ions. Thus, if the central chloride ion is chosen in the square on the face of Fig. 19, it is seen that in this plane it is surrounded by four sodium ions. If another plane is passed through its center at right angles to the front face, there would be one sodium ion in back and one in front (if the lattice were completed), in addition to the top and bottom ones already included in the first plane. The total number of sodium ions surrounding each chloride ion is thus seen to be six. There are no individual NaCl molecules in the sodium chloride crystal. In fact, the concept of molecules is not applicable to this type of crystal lattice. If the term molecule is applied at all, it might be used with reference to the whole crystal. Some types of crystals, however, as in the case of solid carbon dioxide, do have groups of atoms like molecules for the units of their crystal lattices.

Lattice Units in Crystals. The crystal structure of sodium chloride has been worked out in detail to illustrate the use of X rays in determining the type of lattice. In general, the analysis of the structure of a crystal involves assignment to a particular type of symmetry, cal-

culation of the distances in the lattice structure, and determination of the number of atoms in a unit cell. There are 230 different symmetry groups to which the crystal may belong, and the decision as to the correct structure is based on the angles of X-ray reflections and the relative intensities.

The particular crystal structure which will be taken by a given element or compound depends partly on the size of the ion and on the charge of the nucleus, that is, the atomic number as described on page 621. The ions may be composed of single atoms or of groups of atoms. There are different standard types of structure for elements where all atoms are the same and for compounds such as AB, AB_2, AB_3, and others.

The three types of cubic crystals, simple, face-centered, and body-centered, were shown in Figs. 15, 16, and 17, and an example of interpenetrating face-centered cubic lattices was shown in Fig. 19. A few other typical unicells are shown in **Fig. 20.** Several of these units should be stacked up along the three axes in space in order to bring out the full character of the lattice.

The *cesium chloride* (CsCl) type of lattice consists of two interpenetrating simple cubic lattices. Each cube of eight chloride ions has at its center a cesium ion, and, likewise, each cube of eight cesium ions has at its center one chloride ion. The result is a lattice structure with each ion equidistant from eight other ions of the opposite charge.

The *zinc sulfide* (ZnS) lattice is somewhat like the sodium chloride lattice in that it consists of two interpenetrating face-centered cubic lattices. The crystal structure of the *diamond* is of the same lattice type except, of course, that all the atoms of the whole lattice are of the same kind. Each carbon atom is surrounded by four other carbon atoms in the tetrahedral arrangement for carbon familiar in organic chemistry. Four tetrahedrons of the crystal lattice meet at every carbon atom, except at the surface, making a continuous lattice, so that the crystal may be regarded as one large molecule.

In the *cuprous oxide* (Cu_2O) arrangement, the oxygen atoms are arranged on a body-centered cubic lattice, and the cube can then be divided into eight smaller cubes, each touching the central atom at one corner. The copper atoms are arranged on a lattice which penetrates the oxygen lattice so that the copper atoms come at the centers of the alternate small cubes.

The *rutile* (TiO_2) lattice illustrates the tetragonal lattice in which only two of the axes are of the same length.

The *close-packed hexagonal* lattice is another example of a lattice which is not cubical. It is obtained by placing together six prisms

having equilateral triangles as bases. Seven atoms are placed at the top and bottom hexagons thus formed, and three additional atoms are placed in the centers of alternate prisms. Hexagonal close packing is one of the stable ways in which hard spheres can be forced close together. The structure is similar to that in which three spheres touch to form a triangle; a single sphere is piled on top, then another group of three, and so on. Thus, alternating layers of three and one are built up. This structure is found in several metals.

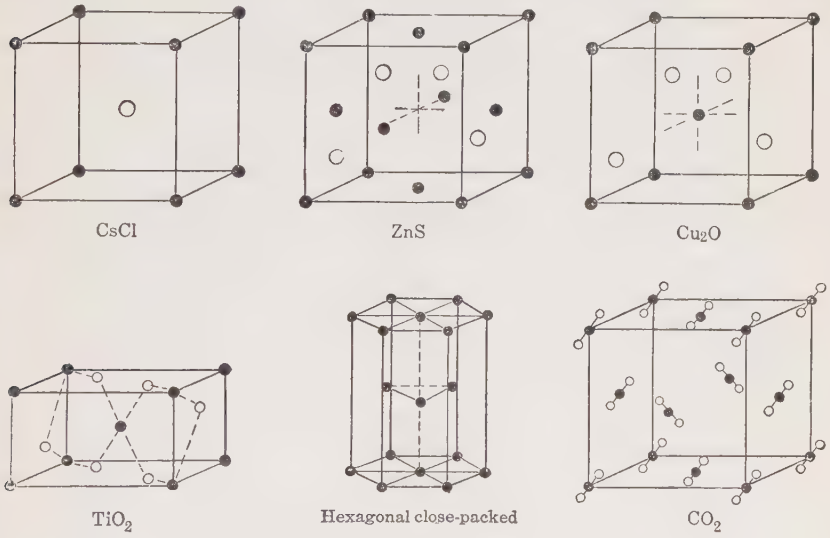


FIG. 20. Some typical crystal lattices.

The units of a crystal lattice are not necessarily atoms or monatomic ions. They may be molecules, as, for example, in *carbon dioxide* (CO_2), where a carbon atom is joined firmly to two oxygen atoms and placed at the eight corners and at the centers of six faces of a cube. The forces holding these molecular crystals together are very weak. The carbon dioxide crystal, for example, is stable only at low temperatures, and, when it vaporizes, the atoms in a given molecule stay together as a unit. Many of the low-melting organic compounds are of this molecular type. In the ionic lattices, such as sodium chloride, there is no union to form molecules in the crystal.

Still another type of lattice, not shown in Fig. 20, is represented by calcium carbonate, sodium nitrate, and other salts. Three oxygen atoms are closely held by carbon atoms, giving carbonate ions which occupy definite positions as units in the crystal lattice. The calcium ions fill up the remainder of the lattice. A carbonate ion does not "be-

long" to a given calcium ion, but three particular oxygen atoms belong definitely to a given carbon atom.

Binding Forces in Crystals. There are two fundamentally different types of attractive forces which hold atoms firmly together and several types of weaker forces which hold molecules together, as explained in Chapter III, the ionic or electrostatic attraction giving rise to heteropolar bonds and the electron-pair bonding or exchange energy giving rise to homopolar bonds.

Many crystals, including all the crystalline salts, give electrically conducting liquids when melted or dissolved, and it is natural to assume that the ions which produce this electric conductivity actually existed as charged ions in the crystal lattice. This view is supported by adequate experimental evidence.* Although the X-ray analysis of crystalline sodium chloride proved that the sodium and chlorine exist as separate units, it did not permit a distinction between their existence as neutral atoms or as charged ions. However, the absolute distance between units in the crystal lattice has been determined by X rays and compared with the radius of the atom and the radius of the corresponding ion as determined by other means. It has been found that in sodium chloride and crystalline salts, in general, the distance between ions in the lattice corresponds to the ionic radius rather than to the atomic radius.

Another convincing argument for the ionic lattice of certain crystals depends on the lattice energies as determined from the heat of formation and heat of evaporation. The energy required to separate the units in the crystal lattice agrees with that calculated on the assumption that the units are ions which are held together by electrostatic forces. Still another argument depends on measurements of the magnetic susceptibilities of the crystals. Since the magnetic effect is considerably greater for ionic bonds with their transferred electrons than for covalent bonds, it is possible to determine the type of binding which exists in the crystal. Measurement of most of the simple crystalline salts indicates that ionic binding is present. Other lines of evidence which indicate the ionic type of binding include measurements of light absorption and dielectric constant.

Although the heteropolar and homopolar bonds account for many crystals and for the formation of chemical compounds from atoms, the additional concepts of electrostatic attraction mentioned in Chapter III are needed to explain the attraction which exists between mol-

* Friedman and Shuler, in *J. Chem. Education*, **24**, 11 (1947), have summarized the experimental evidence for the ionic structure of such crystals, making use of seven different types of measurements.

ecules. This intermolecular attraction due to dipole attraction accounts for the liquefaction of gases and for the formation of many crystals, particularly those which have low melting points like the carbon dioxide shown in Fig. 20.

Structure and Properties of Crystals. Many of the properties of crystals can be predicted from classification of the crystal lattice and the type of binding. The geometrical arrangements obtainable from the crystal lattice have been discussed earlier in the chapter; now the lattice forces give additional information. There are four main types of crystals as follows:

1. The *ionic* type with electrostatic binding is common in many salts. Sodium chloride is a good example. The ions of opposite charges are held together with strong forces which can withstand considerable thermal agitation. The crystals then are strong and possess fairly high melting points. The electrostatic attraction applies only to adjacent and oppositely charged ions. There is no fixed directed force of attraction. The crystal planes will strongly resist any tendency to slip past each other, but, if sufficient external force is applied to move the planes slightly so as to displace the positive–negative ion positions, the force may be greatly weakened. Accordingly, although the ionic crystals are strong, they are apt to be brittle. They have very little elasticity and cannot easily be bent nor worked.

2. The *homopolar* type of crystal with electron-pair bonds is very strong and hard and possesses a very high melting point. Diamond and zinc sulfide are examples of this type. The valence bonds are fixed and rigid, and large external forces are necessary to overcome the attraction which each atom has for all its neighboring atoms. As in the case of the ionic crystals, there are no larger groups of atoms that differ from the fundamental units of which the lattice is made, so that the whole crystal may be regarded as the molecule.

3. The *metallic* type of crystal has atoms all of the same kind, and it is possible for atoms to move around slightly. Accordingly, the metals can be bent and worked. Although they are often less hard than the two preceding types, they are strong and much better able to withstand mechanical and thermal strains. In the metallic crystal the electrons are held loosely, and as a result the crystals are good conductors of electricity.

4. The *molecular* type of crystal has a lattice which consists of molecules held together by weak dipole interaction or van der Waals' forces. Examples are carbon dioxide, carbon tetrachloride, argon, ice, and most organic compounds. Because the lattice forces are weak, the crystals are soft and possess comparatively low melting points. Most of the

substances which have to be cooled below room temperature in order to crystallize are of this molecular type.

In addition to lattice force and lattice type, ionic size is important in interpreting the behavior of crystals. In the larger atoms the outer electrons are situated farther from the positive nuclei of the atoms and are more easily removed and, thus, require less energy for ionization. Again, the structural pattern of the lattice is profoundly influenced by the size of the atoms and ions. For example, in crystals of AB_2, the rutile type of lattice is formed when the ionic radius of A is 43 per cent of that of B; but, when it is 67 per cent, the crystal lattice is of a different type. The density and strength of metals and other materials are closely connected with the type of crystal lattice.

The face-centered and the hexagonal close-packed crystals give arrangements of greatest density with the atoms closest together. If a pile of hard spheres of the same diameter is compressed into the smallest possible space, the packing is likely to follow one of these two arrangements. The elements, which have but one kind of atom, usually tend to crystallize in these forms.

In isomorphous crystals one ion can replace another, but such a displacement is possible only when the crystal lattices are of the same type and the ionic radii are of approximately the same magnitude.

The great difference between graphite and diamond can be understood in terms of the crystal lattice. In diamond every carbon atom is equidistant from four other carbon atoms, and the crystal is hard and perfect. Graphite has hexagonal networks in sheets resembling benzene rings of organic chemistry. The distances between atoms in the plane is 1.4 A, but the distances between these atomic layers is 3.41 A. In two directions, then, the carbon atoms are tightly held as in the diamond, but in the third direction the force of attraction is much less. This gives a structure such that one layer can slip over another. The crystals are less perfect and flaky, and yet the material is not wholly disintegrated under mechanical rubbing. It is excellent then as a lubricant. Other lubricants are also found to have a layer crystal structure.

Determination of the Wave Length of X Rays. Measurements of the diffraction of X rays by crystals can be used in a qualitative manner, as already described, to establish the type of lattice for a given crystal. They can be used also to determine quantitatively the distance between planes when the wave length of the X rays is known; and, conversely, they can be used to determine the wave length of the X rays from the distance between planes when these can be determined independently.

The distance between planes can be calculated from physical dimensions of the crystal and a knowledge of the number of ions which are

associated with each unit of the crystal lattice. In the case of the face-centered cubic lattice of chloride ions, each of the ions at a corner of a cube supplies a corner ion for seven other cubes; that is, each corner ion is shared by eight cubes stacked together so that only one eighth of each belongs exclusively to one unit cell. There are eight such corner ions, each contributing an eighth of its mass to the unit cell so that on the average there is one chloride ion for each unit cube of the chloride-ion lattice. Each unit cube of the chloride lattice also has one ion on each of its six faces which is shared by an adjacent cube so that half of the six ions, or three, can be attributed to a given cube. On the average then, each unit cube of the chloride ion lattice has $1 + 3$ or 4 chloride ions associated with it.* By the same reasoning, each of the unit cells of the sodium-ion lattice also is associated with four sodium ions.

The density of sodium chloride is 2.163, and, accordingly, a mole occupies $58.45/2.163$ or 27.0 cm^3. According to the Avogadro constant, it contains 6.02×10^{23} chloride ions. Four of these ions are associated with each unit cell of the chloride lattice, so that there are $(6.02 \times 10^{23})/4$ unit cells, and the volume of each is

$$\frac{27.0}{\frac{6.02 \times 10^{23}}{4}} = 179 \times 10^{-24} \text{ cm}^3$$

The length of one edge of the unit cube of the chloride lattice is found by extracting the cube root of 179×10^{-24} or 5.64×10^{-8} cm. The same length can be calculated also for the unit cell of the sodium-ion lattice.

Since the interpenetrating lattices of the chloride and sodium ions occupy the same over-all crystal volume, the distance between (100) planes will be half the length of a unit cube of the chloride or sodium lattices; that is, $(5.64 \times 10^{-8})/2$ or 2.82×10^{-8} cm.

Turning now to equation 2, substituting this value for d, and using the angle of the first-order reflection from the (100) plane shown in Fig. 19, we have

$$n\lambda = 2d \sin \theta$$

$$1\lambda = 2d \sin 5.9^\circ = 2 \times 2.82 \times 10^{-8} \times 0.103$$

$$\lambda = 0.581 \times 10^{-8} \text{ cm}$$

X rays are expressed in angstroms, one angstrom A being equal to 10^{-8} cm. The wave length of the X rays generated by the electron bombardment

* This number of chloride ions in the chloride lattice unit is not to be confused with the number of sodium ions surrounding a single chloride ion discussed earlier.

of the palladium target at a given voltage in these experiments is thus shown to be equal to 0.581 A. The same value can be calculated using the measurements obtained with the maximum intensities reflected from the (110) or the (111) planes with either the first-, second-, or third-order reflection. Once the wave length of the rays has been determined, it is possible, with the help of the relation $n\lambda = 2d \sin \theta$, to calculate the distance between planes of any other crystal for which angles of maximum reflection have been determined.

The wave lengths of X rays can also be determined by diffraction of X rays from ruled gratings, if the angles of incidence θ and reflection ϕ are very small, that is, less than 1°. Then,

$$n\lambda = d(\cos \theta - \cos \phi)$$

where d is the distance between the lines mechanically ruled on the face of the grating. After wave lengths have been obtained in this way, the calculation given in the preceding paragraphs can be reversed to give Avogadro's number. In fact, the value of Avogadro's number now considered most accurate is obtained by application of this procedure to calcite crystals ($CaCO_3$).

X-Ray Analysis of Crystalline Powders. In the Bragg method of X-ray analysis, a movable ionization chamber and a large mounted crystal were used to determine the position and intensity of the reflection maxima. Sometimes a strip of photographic film is substituted for the ionization chamber. It is then necessary to rotate the crystal by some type of clockwork mechanism so that the planes of the crystal lattice are sure to be set at the proper angle during part of the time in order to record the maxima in the reflection. Instead of reflecting X rays from a single large crystal, it is convenient to pass the X rays through a large number of small crystals oriented in random directions, as proposed originally by Hull and by Debye and Scherrer. The beam of X rays then gives lines on a photographic plate which are spaced at distances determined by the characteristics of the crystal lattice from which they have been reflected. Some of the small crystals will be oriented so as to give maximum reflections from the (100) planes, and others will give reflections from the (110) and the (111) planes. Many of the crystals, however, will not lie in the proper directions to give these reflection maxima, and they will give rise to interference of light reflected from the different layers and will not register on the photographic plate.

The powder method is very simple, and it has the advantage that only a few milligrams of crystalline material is needed for a measurement. Typical powder X-ray spectrograms obtained by Professor M. L. Jack-

son and Mr. R. P. Pennington of the University of Wisconsin are shown in Fig. 21.

Applications of X Rays. Figure 21*A* is a spectrogram of precipitated calcium carbonate and *B* is a spectrogram of a powdered calcite crystal. The fact that they are the same proves that the calcite is calcium carbonate and that the chemically prepared calcium carbonate has the

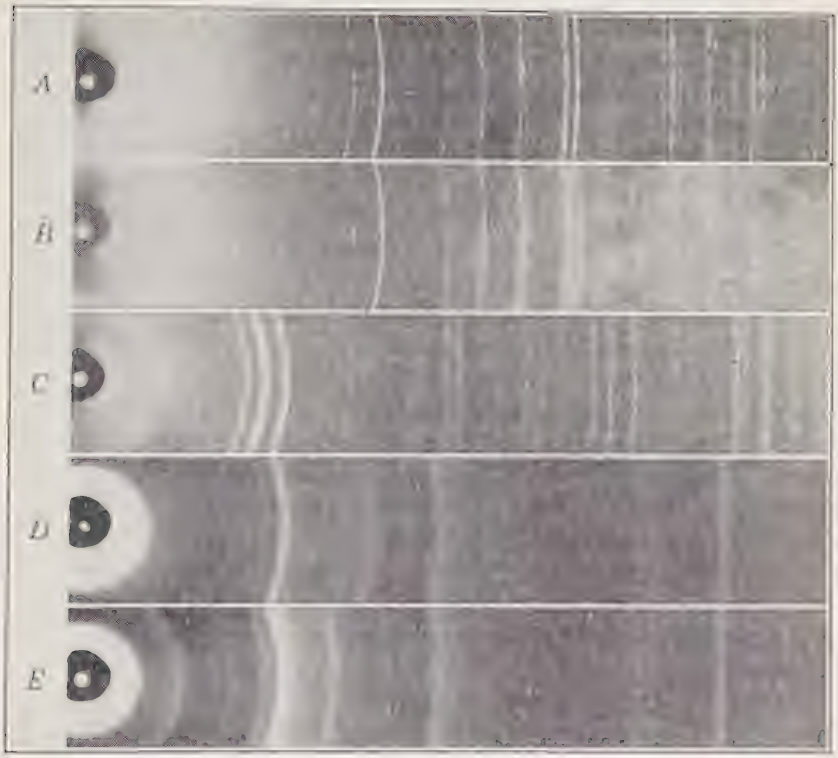


FIG. 21. X-ray powder spectra. *A*. Precipitated calcium carbonate. *B*. Calcite. *C*. Gibbsite. *D*. Clay solvated with water. *E*. Clay solvated with glycerol.

crystal lattice of calcite. The presence of more clearly defined diffraction lines in Fig. 21*A* than in *B* indicates that the calcite structure was somewhat distorted in the process of grinding into powder.

Figure 21*C* is a spectrogram of crystals taken from the soft interior of bauxite. It shows that the formula for bauxite $Al_2O_3 \cdot 2H_2O$ is only an approximation for a physical mixture of gibbsite $Al_2O_3 \cdot 3H_2O$ with less hydrated material.

Figures 21*D* and 21*E* illustrate the use of X rays in studying the behavior of certain clays of interest in the study of soils. They are mon-

plex aluminum silicates with a layer lattice capable of holding an adsorption layer of water or polar organic compounds between the layers. Figure 21*D* shows the clay treated with water and *E* treated with glycerol. Although some of the lines are identical, others undergo interference, depending on the magnitude of the initial spacing, a fact which is helpful in studying the adsorptive properties of these clays.

In organic chemistry the long chains and benzene rings which have been used in structural formulas now find experimental support from the data of X rays. As more CH_2 groups are added to a chain, the length of the crystal unit increases approximately 1.3 A for each carbon atom, but the cross section remains nearly constant. The hydrocarbon $C_{17}H_{36}$, for example, has a length of 24.3 A in the crystal lattice, whereas the hydrocarbon $C_{35}H_{72}$ has a length of 47.7 A.

Crystals which have only a slight degree of symmetry are difficult to interpret with X rays, because the crystals are poorly formed and the planes ill defined. In the examination of organic compounds and crystals containing light elements it is desirable to use soft X rays produced with a target of copper or other light metal, because the X rays produced by targets of heavy metals are too penetrating.

X-ray absorption varies with the density of the absorbing solid. A dense object leaves a shadow on a photographic plate or fluorescent screen. This property is utilized in the setting of broken bones, the extraction of teeth, the removal of bullets, the exploration for abnormal growths, and the examination of the chest for evidences of tuberculosis. The detection of smuggled diamonds, the search for stray metallic objects in food products, and the examination of oranges for frost injury before packing are among the many miscellaneous uses to which X rays are put.

Many metallurgical operations can now be studied more scientifically through the use of X rays. Different crystal forms produced by different heat treatments are readily recognized. Iron carbide in molten iron, for example, when cooled slowly, shows lines which are not present when it is cooled rapidly. A given alloy or material can be standardized by means of X rays, the desired product always giving the same pattern.

Parts of machinery and special metals which are critically important, such as propellers for airplanes, driving shafts for engines, valves for corrosive liquids, and metal parts for large dams, are examined with X rays to insure the absence of structural flaws such as internal fractures or blowholes in castings.

Even material which is not ordinarily classed as crystalline may be tested with X rays, for example, fibers, rubber, shellac, cellulose compounds, and asbestos. A photograph through a pinhole with monochro-

matic X rays gives concentric rings for powders and symmetrical arcs for fibers.

In mineralogy and in chemistry the X-ray spectrum of an unknown material serves as an excellent means of identification, because the X-ray spectra are recorded for most of the minerals and compounds, and a comparison can be easily made. The presence of impurities is easily detected also by additional lines on the photographic plate, and the percentage of these impurities can be estimated by comparing the intensities of the lines with a series of spectrograms taken under identical conditions but containing known amounts of the impurity. The X ray is finding important application also in soil analysis, because it gives important information easily and quickly concerning the mineral constituents which are present.

X-ray analysis has also been of great help as a research tool in inorganic chemistry. For example, in the study of the new man-made elements, neptunium, plutonium, curium, and americium, it was possible to establish quickly the purity of compounds and the chemical composition with exceedingly small amounts of material and without destroying the samples.

REFERENCES

Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., New York, 1940.

Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939.

Wyckoff, "The Structure of Crystals," Second Edition, Chemical Catalog Co., New York, 1931.

Zachariasen, "Theory of X-Ray Diffraction in Crystals," John Wiley & Sons, New York, 1945.

Reinmuth, Some Elementary Principles of X-Ray Crystal Analysis, *J. Chem. Education*, **7**, 138, 860, 1373 (1930).

Stillwell, Crystal Chemistry, *J. Chem. Education*, **10**, 590, 667 (1933); **11**, 159 (1934); **13**, 415, 469, 521, 566 (1936); McGraw-Hill Book Co., New York, 1938.

Evans, "An Introduction to Crystal Chemistry," Cambridge University Press, Cambridge, 1939.

Clark, "Applied X-Rays," Second Edition, McGraw-Hill Book Co., New York, 1932.

Davey, "The Study of Crystal Structure and Its Applications," McGraw-Hill Book Co., New York, 1934.

PROBLEMS

1. A certain crystal face intercepts the X axis at $\frac{1}{2}a$, the Y axis at b, and the Z axis at $\frac{2}{3}c$. What are the Miller indices of this face? *Ans.* 4, 2, 3.

2. In the reflection of X rays of wave length 0.643 A by a certain crystal, first-order maxima for the (100), (110), and (111) planes are obtained when θ is 7° 41′, 5° 26′, 13° 34′, respectively. (*a*) What are the values of d_{100}, d_{110}, and d_{111}, and (*b*) what type of lattice has this crystal?

Ans. (*a*) $d_{100} = 2.40 \times 10^{-8}$ cm. (*b*) body-centered cubic.

3. Potassium bromide has a lattice which is equivalent to a face-centered cubic lattice, and the edge of the unit cube is 6.54 A. The unit contains the equivalent of 4 ions of each kind. What is the density of the crystal? *Ans.* 2.83.

4. Cesium bromide crystallizes as if it were a body-centered cubic. In the Bragg spectrometer using X rays of 0.576 A a first-order maximum for the (100) plane is obtained at an angle of θ of 7° 43′. What is the interplanar distance d_{100}? The length of the unit cell is $2 \times d_{100}$, and it contains the equivalent of one molecule of CsBr. What is the density of the cesium bromide? *Ans.* 4.49.

---

5. The Miller indices of three faces of a cubic crystal are (100), (010), and (001).

(*a*) What are the intercepts of the three faces?

(*b*) Sketch the crystal showing these three faces.

6. Potassium crystallizes with a body-centered cubic lattice. The density is 0.8560 g per cubic centimeter. Calculate the distances (*a*) between (100) planes, (*b*) between (110) planes and (*c*) between (111) planes.

7. Calcium oxide was examined with X rays having a wave length of 0.576 A. First-order maxima were observed for the (100) plane at $\theta = 6° 54'$, for the (110) plane at 9° 52′, and for the (111) plane at 6° 00′. What are the values of d_{100}, d_{110}, and d_{111}, and what type of lattice does this crystal have?

8. A substance crystallizes in a form like that of sodium chloride. Its density is 1.984 g per milliliter and its molecular weight is 74.56. What is the length of the edge of a single cell?

9. The crystal unit cell of MgO is a cube 4.20 A on an edge. Each cell contains the equivalent of 4 atoms of magnesium and 4 of oxygen. What is the density of crystalline magnesium oxide?

10. Copper is a face-centered cube in crystalline form, with the dimensions $a = b = c = 3.608$ A. Calculate its density.

---

11. The diamond has a crystal lattice which is face-centered cubic, and there are 8 atoms in a unit cell. Its specific gravity is 3.51. What possible reflection angles could be found for the diamond crystal from the (100), (110), and (111) planes with an X-ray beam of wave length 0.712 A? Reflections have been observed at $\theta_{100} = 23° 40'$, $\theta_{110} = 16° 20'$ and $\theta_{111} = 10° 0'$ with maximum intensities. Do these data indicate a first-, second-, or third-order reflection?

12. Metallic iron investigated with monochromatic X rays from an unknown source at 20° gave first-order reflection maxima when $\theta = 11° 36'$, 8° 3′, and 20° 26′ in the (100), (110), and (111) planes, respectively. At 1100° the maxima occurred when $\theta = 9° 8'$, 12° 57′, and 7° 55′.

(*a*) What do these results show concerning two crystalline modifications of iron which are stable at these two temperatures?

(*b*) Calculate d_{100} for the 20° form. The density of iron at 20° is 7.86.

(*c*) Calculate the wave length of the X rays used.

(*d*) What is the density of iron at 1100°?

CHAPTER V

PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

A physical property, such as molecular weight, which depends on the number and kind of atoms in the molecule is called an *additive* property. A physical property, such as the optical rotation of light, which depends on the particular arrangement of atoms within the molecule is called a *constitutive* property. A great many physical-chemical properties are additive in part and constitutive in part. The prediction of physical properties from the known constitution is valuable from both a practical and a theoretical viewpoint. Likewise, these physical properties are useful in identifying chemical substances and deciding questions of their molecular structure.

The rigid bonds which hold organic molecules together make definite constitutions possible, whereas the mobility of ions in solution prevents a definite spatial structure. This chapter, therefore, is concerned chiefly with the materials of organic chemistry.

Refractive Index. The extent to which a beam of light is bent or refracted when it passes from one substance into another depends on the relative number of atoms in the two substances which are in the path of the light (that is, on the concentration), on the kind of atoms, and on the arrangement of atoms within the molecules. Accordingly, the refractive index, which is a quantitative measure of this refraction of light, may be used to determine concentration of materials, to establish the identity and purity of a chemical compound, or to ascertain the arrangement of atoms within the molecule.

When a beam of light passing through one substance strikes the surface of a second substance, the direction of the beam is changed. The angle of incidence i is the angle which the oncoming beam makes with a line perpendicular to the surface which separates the two substances, and the angle of refraction p is the angle which the diffracted beam, traveling in the second substance, makes with reference to a line perpendicular to the surface. The index of refraction n is then defined by the equation,

$$n = \frac{\sin i}{\sin p} \tag{1}$$

The index of refraction can be defined also as the ratio of the velocities of light in the two substances. Usually the *refractive index* given in the tables refers to the index of refraction measured when the light emerges from the substance into air. Because the refractive index of air itself changes with the temperature, pressure, and humidity, the *absolute refractive index* has been established as the ratio of the velocity of light in a vacuum to the velocity of light in the given medium. The ordinary refractive index measured in air can be converted into absolute refractive index by multiplying by the refractive index of air, which is about 1.00029 under standard conditions.

The experimental measurements of refractive index is one of the easiest and most accurate measurements of physical chemistry. It can be determined easily to two parts in 10,000 under laboratory conditions where the temperature is carefully controlled. In making a refractive-index measurement, the beam of light is usually passed from air through the solid or liquid medium being measured and then through a glass prism and out into the air again. The refractive index may be calculated from the angle through which a telescope must be turned in order to pick up the emerging beam on a cross-hair. The angle measured includes the refraction at the liquid–glass interface and at the glass–air interface, so that a calculation (shown in the appendix on page 674) is necessary to obtain the refractive index of the liquid against air.

In some refractometers the angle of the emerging light beam is read on a scale which is calibrated not in degrees but directly in refractive index—a procedure justified by the fact that the refractive index of the glass prism against air is a constant.

The index of refraction depends on the wave length of the light employed, the refraction for the red being less than that for the violet light. The wave length of the light used in measuring the refractive index n is recorded as a subscript. Measurements of the refractive index are often referred to the D line of sodium, 5893 A, but sometimes the green mercury line at 5461 A, or the lines of the hydrogen spectrum H_α, H_β, or H_γ are used as the source of light. The temperature at which the measurements are made is indicated by a superscript. Thus the symbol $n_D^{25^\circ}$ refers to the refractive index measured at 25° with sodium light. Monochromatic light is used for the greatest precision, but white light may be used if a compensating prism is adjusted so as to eliminate any color fringe. Because the angle of refraction changes with the wave length to a different extent for each substance, it is necessary to adjust such a compensator for every substance measured.

The refractive indices of several different substances are given in Tables I and II.

TABLE I

Refractive Indices with Different Wave Lengths of Light

Compound	Formula	n_D^{20} [1]	$n_{H_\alpha}^{20}$	$n_{H_\beta}^{20}$	$n_{H_\gamma}^{20}$
Thenardite	Na_2SO_4	.....	1.464	1.474	1.485
Tridymite	SiO_2	.....	1.469	1.47	1.473
Formic acid	CH_2O_2	1.37137	1.36927	1.37643	1.38041
Ethyl bromide	C_2H_5Br	1.42386	1.42113	1.43046	1.43595
Benzene	C_6H_6	1.50144	1.49663	1.51327	1.52361
Aniline	C_6H_7N	1.58629	1.57948	1.60434	1.62074
n-Propyl alcohol	C_3H_8O	1.38543	1.38345	1.39008	1.39378
Nitrobenzene	$C_6H_5NO_2$	1.55291	1.54593	1.57124	.....

[1] In refractive index the superscript specifies the temperature.

Molar Refraction. The refractive index of a fluid varies with temperature and pressure as the number of molecules in the path of the light is changed, but the *specific refraction* r is quite independent of these variables. On the basis of the electromagnetic theory of light, Lorenz and Lorentz have shown that

$$r = \frac{1}{d}\frac{n^2 - 1}{n^2 + 2} \qquad (2)$$

where n is the refractive index and d the density. The *molar refraction* is equal to the specific refraction multiplied by the molecular weight.

Example 1. The refractive index n_D of allyl alcohol at 20° is 1.41345, the density at 20° is 0.8540, and the molecular weight is 58.078. Calculate the molar refraction.

$$Mr_D = \frac{M(n^2 - 1)}{d(n^2 + 2)} = \frac{58.078\,(1.41345^2 - 1)}{0.8540\,(1.41345^2 + 2)}$$

$$= \frac{58.078 \times 0.99784}{0.8540 \times 3.99784} = 16.97$$

The refractive index at 20°, the specific refraction, and molar refractions are given for several common liquids in Table II.

The refraction of light is an additive property, but it is also partly a constitutive property depending on the structural arrangement of the atoms within the molecule. The molar refractions of a large number of organic and inorganic compounds have been determined, and it has been found that many atoms and groups of atoms always contribute

the same definite amount to the molar refraction of any compound in which they are found. Thus, in a homologous series of aliphatic compounds a difference of CH_2 in composition always produces a difference of 4.618 in the molar refraction. The molar refraction of hexane,

TABLE II

Molar Refractions

Compound	Formula	n_D^{20}	r_D^{20}	Mr_D^{20}
Carbon tetrachloride	CCl_4	1.4573	0.1724	26.51
Acetone	$(CH_3)_2CO$	1.3571	0.2782	16.15
Benzene	C_6H_6	1.4979	0.3354	26.18
Ethanol	C_2H_5OH	1.3590	0.2775	12.78
Toluene	$C_6H_5CH_3$	1.4929	0.3356	30.92
Chloroform	$CHCl_3$	1.4426	0.1780	21.25
Acetic acid	CH_3COOH	1.3698	0.2154	12.93
Ethyl acetate	$CH_3COOC_2H_5$	1.3701	0.2527	22.25
Water	H_2O	1.3328	0.2083	3.75

C_6H_{14}, is 29.908, and, by subtracting from this value six times the effect of the CH_2 group, it is possible to obtain the atomic refraction of the hydrogen atom, namely, 1.100. Thus,

$$\frac{29.908 - (6 \times 4.618)}{2} = 1.100$$

From these data the atomic refraction of carbon is readily calculated, thus:

$$4.618 - (2 \times 1.100) = 2.418$$

Again the atomic refraction of bromine is obtained by subtracting the atomic refractions of two carbons and five hydrogens from the molar refraction of ethyl bromide.

The atomic refractions are affected by the structural features. For example, the molar refraction of $BrH_2C - CH_2Br$ is 26.966 and the molar refraction of $BrHC = CHBr$ is 26.499.* If the atomic refractions of the hydrogen and bromine atoms are subtracted, the value for $C - C$ is 4.836, and for $C = C$ it is 6.569. Since the two carbons together have a value of 4.836, it follows that a double bond between carbon atoms contributes an additional 1.733 to the molar refraction.

* The experimental values available in the literature give 27.0 and 26.3.

Table III has been built up in the manner just indicated, averaging the results for a large number of compounds.

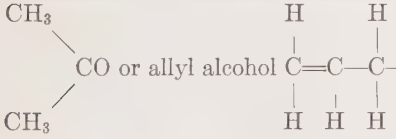
TABLE III

ATOMIC REFRACTIONS

Group	Mr_D	Group	Mr_D
CH_2	4.618	Cl	5.967
H	1.100	Br	8.865
C	2.418	I	13.900
Double bond (C=C)	1.733	N (pri-amines)	2.322
Triple bond (C≡C)	2.398	N (sec-amines)	2.499
O (carbonyl) (=CO)	2.211	N (tert-amines)	2.840
O (hydroxyl) (—OH)	1.525	C N	5.459
O (ethers) (R—O—R)	1.643		

This table is useful in determining the structure of molecules as it enables one to select the atom or group of atoms with the proper structural features so that the sum of the atomic refractions will add up to give a total which is equal to the experimentally determined molar refraction.

Example 2. A substance having the analysis C_3H_6O might be either acetone



CO or allyl alcohol $CH_2=CH-CH_2-OH$. Determine which of these two substances it is from the fact that the molar refraction Mr_D is 16.974.

Acetone		Allyl Alcohol	
3 carbons	= 7.254	3 carbons	= 7.254
6 hydrogens	= 6.600	6 hydrogens	= 6.600
1 carbonyl oxygen	= 2.211	1 double bond (C=C)	= 1.733
	16.065	1 hydroxyl oxygen	= 1.525
			17.112

Since the experimentally determined molar refraction agrees with that calculated for allyl alcohol, the substance is allyl alcohol rather than acetone.

Rotation of Polarized Light. Ordinary light can be *plane-polarized* by passing it through a Nicol prism or a "Polaroid" film with the result that the electromagnetic vibration of the transmitted light is confined

to a simple plane. A Nicol prism consists of a crystal of doubly refracting Iceland spar cut and cemented in such a way that one of the rays is refracted to one side and the remaining one which passes through is plane-polarized. Polaroid films are made by incorporating into a transparent plastic a large number of small crystals of a compound, such as an iodide of quinine, which possesses the property of double refraction, and orienting them all in one direction.

When certain optically active substances are placed in a beam of polarized light, the plane of polarization is rotated either to the right or to the left and the extent of this optical rotation is measured quantitatively in a *polarimeter*, the principle of which is shown in **Fig. 22.**

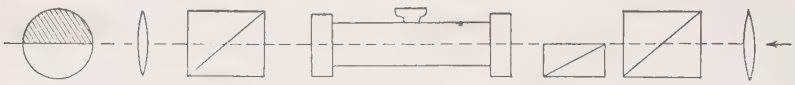


Fig. 22. Diagram showing the principle of the polarimeter.

A beam of monochromatic light is passed through a Nicol prism or other means for producing plane-polarized light; thence, through a tube containing the optically active material; and, finally, through a second Nicol prism. When these prisms are placed at right angles with no optically active material intervening, the only light passed by the first prism is stopped by the second, and the rear field appears dark. When optically active material is introduced, however, the light appears again, and the second prism must be rotated in order to prevent the passage of light. The number of degrees through which the second prism must be rotated, in order to stop the beam of polarized light, is a measure of the optical rotation. For dextrorotatory substances it is necessary to rotate the rear prism to the right; for levorotatory substances it must be turned to the left. It is difficult to know when the second prism has been rotated just far enough to allow the minimum passage of light, and, accordingly, a reference is used to improve the accuracy. An additional Nicol prism or a thin sheet of optically active material is placed behind the first Nicol prism so as to intercept half the field and give a slightly different degree of rotation. When the back Nicol prism is crossed with the unobstructed half of the light from the first Nicol, the other half of the field is lighter, and, when it is crossed with the obstructed half, the unobstructed half becomes lighter. A sharp and reproducible reading is obtained when the second Nicol prism is turned so that both halves of the field are equally illuminated, and the line of demarkation between the two disappears.

The extent of the optical rotation depends on several factors, including the nature of the substance; the length of the column through which the

light passes; the concentration, in case the material is dissolved in a solution; the wave length of the light; and the temperature. Accordingly, it is helpful to employ a term in which the number of these variables is reduced. Fulfilling these requirements is the *specific rotation* defined by the following equation,

$$[\alpha]_{\lambda}^{t} = \frac{\alpha}{l\frac{g}{v}} \qquad (3)$$

where α is the observed rotation in degrees, l is the length of the path in decimeters * of optically active material through which the light passes, and g/v is the number of grams of optically active material g in v milliliters of volume. For solids or liquids g/v is simply the density; for solutions it expresses the concentration of active material. The wave length is recorded as a subscript. The yellow D light of the sodium arc or the intense green light of the mercury arc is usually used in polarimetric measurements. The temperature t does not greatly affect the specific rotation; sometimes it is recorded as a superscript, but, if the temperature is not recorded, room temperature or about 20° is assumed.

The specific rotations are useful for the rapid and accurate analysis of optically active materials, as indicated in the following example:

Example 3. An aqueous solution of maltose containing 13 g in 100 ml was examined in a polarimeter having a cell 20 cm in length and found to have a rotation of 34°. What is the specific rotation of maltose? Another solution of maltose gave a rotation of 42.5° in a cell 10 cm long. What is the concentration in grams per liter?

$$[\alpha]_{D}^{25^\circ} = \frac{34 \times 100}{2 \times 13} = 130.8^\circ$$

$$g = \frac{42.5 \times 1000}{1 \times 130.8} = 325$$

Optical Activity and Molecular Structure. Optical activity is found most often in compounds which contain a carbon atom attached to four different atoms or groups of atoms. Such a carbon atom is called an *asymmetric* carbon atom, one of the simplest examples of which is lactic acid indicated in **Fig. 23.**

The compounds which rotate the plane of polarized light to the right in a clockwise direction as viewed in a polarimeter are called dextro-

* It would be better to express the length in centimeters, as is done with most other physical-chemical properties, but the tables and the literature record specific rotation using decimeters.

rotatory, and those which rotate it to the left in a counterclockwise direction are called levorotatory.

The *molar rotation* $M[\alpha]_\lambda^t$ is obtained by multiplying the specific rotation by the molecular weight M.* The molar rotation $M[\alpha]_D^{25°}$ of sucrose (sugar) is $M \times 66.43°$ in dilute solutions in water and the molar rotation of *d*-glucose is $M \times 52.48°$. If the dextro and levo forms occur together in equal amounts in the same solution, the two rotations offset each other, and no optical activity is observed. Such a mixture is called a *racemic* mixture. As a matter of fact, almost all material which is capable of exhibiting optical activity is found in the racemic form when produced

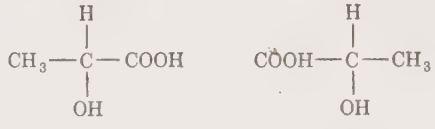


FIG. 23. Structure of levo- and dextrolactic acid.

in the laboratory. In synthesizing lactic acid, for example, there is equal probability of obtaining either the dextro or levo form, and the same numbers of molecules of each are formed.

Although the dextro and levo forms have nearly the same physical and chemical properties, except for the rotation of polarized light, they can be separated. Microorganisms sometimes will destroy one form more rapidly than the other. For example, a certain mold growing in a racemic mixture of tartaric acid will thrive at the expense of the dextro acid and leave the pure levo acid. Other microorganisms, or rather the enzymes which they contain, may consume the levo form and leave the dextro. Most optically active organic compounds are obtained from some plant or animal product or some fermentation process in which slight difference in one of the growth processes, such as solubility or rate of reaction, may be involved. In a second method of separating dextro and levo optical isomers, the racemic mixture is allowed to react chemically with an optically active material which gives products having slightly different solubilities. Optically active alkaloids have been used for separating the *d* and *l* forms of acids. Another method of separating racemic mixtures has been reported in which one component is preferentially decomposed photochemically through the use of circularly polarized ultraviolet light.

Sometimes the two optical isomers crystallize out in crystal forms which are alike except that one crystal form is the mirror image of the

* In the older literature these molar rotations are divided by 100.

other. They can then be separated by hand picking, as was done first by Louis Pasteur in his brilliant researches on the optical activity of tartaric acid.

The magnitude of the rotation is, in part, connected with the relative masses of the atoms or groups of atoms surrounding the central asymmetric carbon atom, and some regularities occur in homologous series. The specific rotation of some solutes is the same in different solvents, but usually it varies in a manner which is specific for each solvent and solute. Apparently some loose combination with the solvent at certain parts of the molecule changes the rotation. Ionization of the optically active molecule usually leads to a marked change in the specific rotation. Optical activity is not restricted to the asymmetric carbon atom; it has been observed in compounds containing asymmetric atoms of nitrogen, sulfur, tin, cobalt, and other elements. Moreover, it has been observed in certain types of organic compounds which contain an unsymmetrical grouping but no asymmetric atom.

Crystals exhibit two different types of optical activity. In some crystals, as, for example, in sugar, the molecules themselves are optically active. In others, as, for example, in quartz, the crystal rotates the plane of polarized light by virtue of a spiral arrangement of the units in the crystal lattice.

Absorption of Light. The mechanism by which light is absorbed by molecules is discussed more fully in Chapters XIX and XX, but it may be stated here that absorption of light in the visible and ultraviolet regions of the spectrum involves the displacement of electrons within the molecules. Absorption in the infrared region where the wave lengths are longer involves the displacement of atoms. According to the quantum theory, a beam of light is composed of many units of radiation called photons. The energy of one photon is called a quantum of energy, and it depends on the wave length of the light, the quantum being large in the ultraviolet, of lesser energy in the blue, and still less in the red and infrared. However, all the photons in monochromatic light of a given wave length have the same energy.

There are only certain displacements of electrons or atoms within the molecule which are permissible according to the quantum theory, and, when the photons in a beam of light passing through a given material happen to have about the same energy as the energy required to bring about a permissible change within the molecule, there is a definite probability that the photon will be absorbed and its energy consumed in effecting the displacement inside the molecule.

When white light or polychromatic light containing many different wave lengths is passed into a substance, some of the light may be ab-

sorbed, the rest being either transmitted or reflected. A substance appears colored because part of the light is absorbed. For example, a solution of copper ions appears blue because, when white light is passed through it, the red and yellow light is absorbed, and only the blue is transmitted to the eye. The colored light, transmitted or reflected, can be measured by passing it through a spectrometer and spreading it out into a spectrum by means of a prism or grating.

In some cases where there is discontinuous absorption, the light will appear as narrow lines of light which are images of the slit of the spectrometer. In most cases the absorption is continuous, and the bright light transmitted extends over a considerable range of wave lengths giving bands instead of lines. Dark regions in the spectrum show that light corresponding to those particular wave lengths is absorbed. An examination of the character and intensity of the absorption spectrum is a method widely used for the identification and determination of the absorbing material.

Absorption in the ultraviolet is measured with the photographic plate; absorption in the visible is readily detected either with the eye or with a photographic plate.* Infrared radiation does not affect the eye, or the common photographic plate, or the ordinary photoelectric cell, and so the absorption spectrum is determined with a sensitive thermopile which absorbs the heat rays and converts them into electricity which is measured with a galvanometer. Near-infrared radiation can be measured with specially sensitized photographic plates. Glass prisms and lenses are satisfactory for visible light, but quartz or fluorite CaF_2 is generally used for the ultraviolet, and rock salt or potassium bromide for the infrared. The apparatus must be transparent to whatever light is being used.

The wave length of light is measured in angstroms. One angstrom,† A, is one hundred millionth (10^{-8}) of a centimeter.

Light is described also in *wave numbers* which are expressed in reciprocal centimeters. For example, ultraviolet light of 2500 A, has a wave length of 2.5×10^{-5} cm and a wave number of $1/(2.5 \times 10^{-5})$ or 40,000 reciprocal centimeters. Strictly speaking, the wave lengths used in calculating wave numbers should be measured in vacuum, and, if desired, the wave length measured in air can be converted to wave length measured in vacuum by multiplying by 1.00029 which is the refractive index of air.

* Apparatus and methods of spectrometry are described in "Experimental Physical Chemistry," by Daniels, Mathews, and Williams, McGraw-Hill Book Co., New York, 1941.

† The millimicron, mμ, which is 10^{-7} cm, is a unit of wave length equal to 10 A. General practice is tending toward its elimination.

The *frequency* of light, obtained by multiplying the wave number by the velocity of light, 3×10^{10} cm sec^{-1}, is important in photochemistry (page 597) and in calculations of energy.

The percentage of light transmitted at a given wave length may be measured in different ways. The spectrum may be photographed with a spectrograph, and the blackening of the plate indicates the wave lengths at which light is transmitted. In this way it is easy to determine at what wave lengths absorption bands occur. The plate is calibrated for wave lengths by comparison with a spectrum of known wave lengths, such as mercury or iron spectrum, taken with the same spectrograph. Over a limited range of exposure, the blackening is directly proportional to the amount of light striking the plate, and an estimate of the intensity of light transmitted at a certain wave length can thus be made. The blackness may be compared directly with an adjacent exposure on the same plate produced in the same length of time by a beam of light whose intensity has been reduced by a definite measured amount using a sector wheel, Nicol prisms, or a wire screen. Also, the density of the spectrogram may be determined quantitatively by passing a narrow beam of light along the plate and measuring with the help of a photoelectric cell or thermopile the light absorbed by different parts of the plate.

The use of photocells in absorption measurements is increasing rapidly in popularity. The deflection of a sensitive galvanometer connected to a photoelectric cell or photovoltaic cell is directly proportional to the light transmitted, and it is not necessary to make a photograph of the spectrum. The light may be divided into short spectral regions by means of filters or by prisms or gratings and the per cent transmission determined for a narrow band of the spectrum.

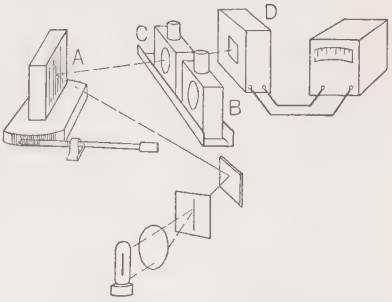


Fig. 24. Spectrophotometer for measuring the absorption of light at different wave lengths.

The principle of such an instrument is shown in **Fig. 24.** A beam of light is passed through a narrow slit onto an optical grating A, from which it is reflected through a cell C containing the solution, and thence to the photocell D which is connected to the galvanometer. The percentage of light transmitted is calculated by dividing this deflection I by the deflection I_0, obtained when cell B containing the solvent is slid along into the path of the light, displacing the cell C. By turning the

screw the grating is turned so as to pass any desired wave length through the cell. In this way the transmission I/I_0 may be determined for the different wave lengths, and the spectrum may be mapped. When the desired absorption band is located, the instrument may be set for this wave length and the transmission determined for different concentrations of absorbing material. The positions of the absorption bands and lines serve for identification and for criteria of purity, whereas the percentage transmissions serve for quantitative analyses of the amount of material present.

Emission spectra of volatilized metals and compounds are readily obtained using an arc, a spark, or a flame, and these are valuable in qualitative and quantitative analysis. In quantitative estimation of the amounts of material, it is necessary to compare the blackening of the plate with the blackening produced by known amounts of the standard substance volatilized and activated under identical conditions of current and voltage.

Lambert's Law. It was stated that the extent of the absorption depends on the probability that the energy of the quantum will be transferred to the molecule where it can effect a chemical reaction or where it is dissipated eventually as heat. It depends also on the number of molecules in the path of the light. This probability is expressed mathematically by the proportionality constant k' in the formula,

$$\frac{dI}{I} = -k'\,dl \tag{4}$$

where I is the intensity of light, that is, the number of photons per second per square centimeter hitting the surface, and dI is the change in light intensity produced by absorption in a very thin layer dl of the absorbing material. A large value of this proportionality constant k' indicates that the material is very absorbing. The value of k' varies with the wave length of light.

At a given wave length the intensity I of transmitted light after the beam has passed through l centimeters of the absorbing medium is related to the initial intensity I_0 by equation 5, which is obtained by integrating * equation 4 between the limits I_0 when $l = 0$, and I at length l.

$$\ln\dagger \frac{I}{I_0} = -k'l \tag{5}$$

* Details of this simple integration are given in Daniels' "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., New York, 1928, page 132.

† ln signifies $\log_e$; log signifies $\log_{10}$; $2.303 \log x = \log_e x$.

Beer's Law. The intensity of transmitted light is affected by a change in the concentration of absorbing material as well as by a change in the thickness of the absorbing material. If the length of the absorbing cell is fixed, Beer's law gives the relation,

$$\frac{dI}{I} = -k'' \, dc \tag{6}$$

where c is the concentration, expressed in moles or grams per liter. Usually equations 4 and 6 are combined giving the Beer–Lambert law,

$$\ln \frac{I}{I_0} = -klc$$

or, in exponential form,

$$I = I_0 e^{-klc} \tag{7}$$

where k is called the *absorption coefficient.*

The equation is such that a straight line is produced when the logarithm of the fraction of light transmitted, I/I_0, is plotted against the concentration of absorbing material when the same absorption cell is used so that the length l is constant.

Equation 7 may be written with logarithms to the base 10, as

$$\log \frac{I}{I_0} = -Elc \tag{8}$$

where E is known as the *extinction coefficient.* When l is in cms and c is in moles per liter, the resulting molar extinction coefficient is sometimes given the symbol ϵ.

Example 4. When a 1.9-cm absorption cell was used, the absorption of blue light by bromine dissolved in carbon tetrachloride was found to be as follows:

Concentration of Br_2 (c) in moles per liter	0.00546	0.00350	0.00210	0.00125	0.00066
Transmission (I/I_0)	0.010	0.050	0.160	0.343	0.570

Calculate the molar extinction coefficient ϵ.

In **Fig. 25,** $\log I/I_0$ is plotted against concentration, and the constant ϵ is calculated from the slope of the line and the thickness of the cell to be 193.

What per cent of the incident light would be transmitted by 2 cm of a solution containing 0.00155 mole of bromine per liter of carbon tetrachloride?

$$\log \frac{I}{I_0} = -\epsilon lc = -193 \times 2 \times 0.00155 = -0.599 = \bar{1}.401$$

$$\frac{I}{I_0} = 0.252$$

That is, 25 per cent of the light is transmitted, and 75 per cent is absorbed, neglecting the amount reflected.

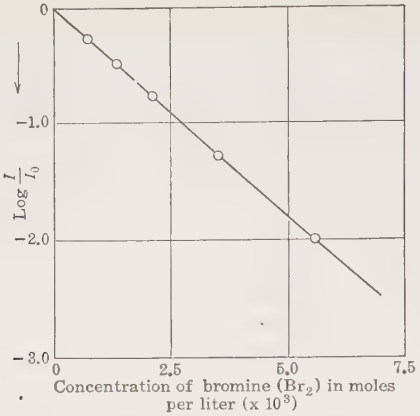


FIG. 25. Graph showing the transmission of light as a function of the absorbing material.

The amount of light absorbed, A, is equal to the difference between the incident light and the transmitted light. Thus,

$$A = I_0 - I = I_0(1 - e^{-kcl}) \tag{9}$$

In this calculation the reflected light is ignored, but it may be estimated. It amounts to about 4 per cent when a perpendicular beam of light goes from air to glass or glass to air.

The absorption of light is widely used now for measuring quickly and accurately the concentration of a colored material.

The transmission of light can be measured visually by comparing the intensity with the intensity of light after passing through a known standard solution in a colorimeter.

In a colorimeter the depth of a known standard solution is adjusted until the intensity of transmitted light just matches, according to the eye, the intensity transmitted by the unknown solution being analyzed. The concentration is readily calculated from the depth of the solutions and the concentrations of the standard solution.

Analysis by the absorption of light has many advantages. It is quick and accurate and can be carried out without disturbing the material or withdrawing a sample. Although it is limited to colored substances, it must be remembered that most substances are colored in the ultraviolet and infrared. Applications in these fields are now receiving attention. In fact, the quantitative analysis of complex mixtures of organic compounds in the cracking of petroleum is now done effectively with the help of absorption spectra at different wave lengths in the infrared.

Absorption and Chemical Structure. The absorption of light may be used not only for determining the concentration of the colored substance but also for identifying it. The spectroscope is very widely used for analysis by emission spectra, but it is used also for absorption spectra. Many ions, dyes, and other colored organic and inorganic substances have characteristic absorption spectra. A ketone group (=C=O), for example, absorbs between 3000 and 4000 A, depending on the adjacent groups, and again in the infrared at 58,000 A.

The absorption of light by a solution changes with the thickness of the layer and with the concentration in a manner which is characteristic for each absorbing material. Sometimes the spectrum is photographed at a number of different thicknesses or at a number of different concentrations, and the region of absorption gradually narrows as the solution is diluted. The wave length of the last part of the absorption band to fade out is characteristic of the absorbing material.

It is often possible to predict the absorption spectra of organic compounds from a knowledge of the structure and the influence of substituted groups. Likewise, the absorption spectra are helpful in deciding questions of chemical constitution. Several spectra, plotted in different ways, are shown in Figs. 26, 27, and 28.

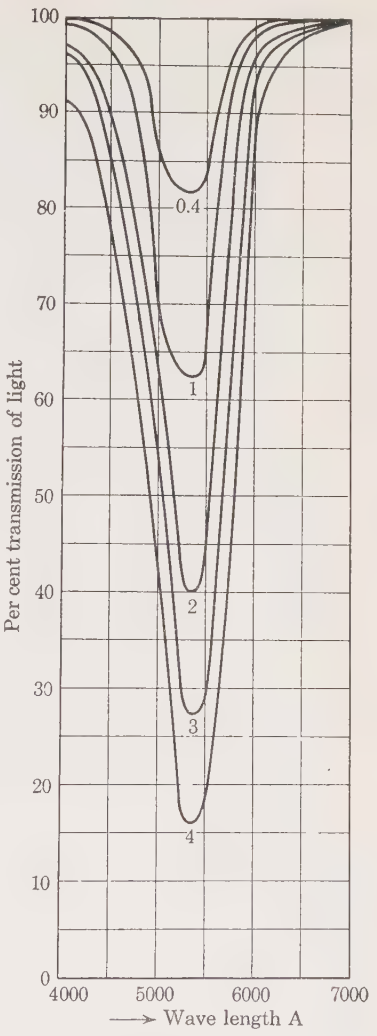


FIG. 26. Absorption spectrum of compound formed with ferrous iron and a dioxime. Numbers 0.4 to 4 indicate parts per million of iron in solution in a cell 1 cm thick.

Figure 26 gives the absorption spectrum throughout the visible of the intensely colored compound which is produced when a solution of ferrous iron is mixed with a certain dioxime.* This colorimetric test is a very

* Griffing and Mellon, *Anal. Chem.*, **19**, 1018 (1947).

sensitive method for testing for ferrous iron, one part per million giving a large change in the amount of light transmitted.

Figure 27 gives an excellent absorption spectrum of chlorophyll from green leaves showing the two components, chlorophyll A and chlorophyll B, with slightly different absorption maxima. This spectrum is adapted from one by Zcheile * obtained with a spectrometer provided with a photoelectric cell.

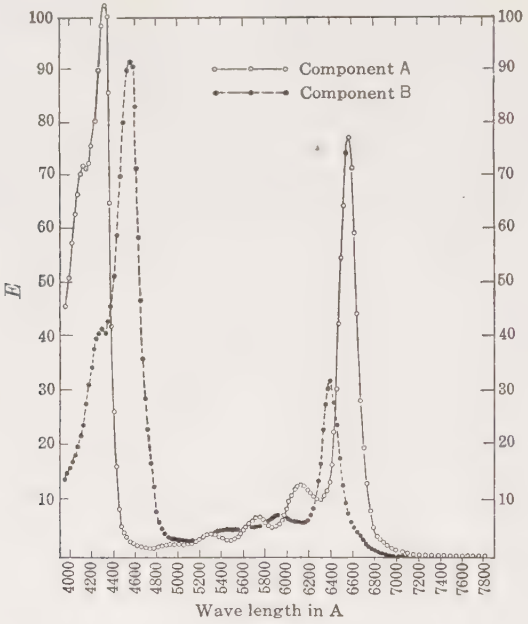


FIG. 27. Absorption spectrum of chlorophyl.

Figures 28*a* and *b* are taken from an investigation on vitamins by Ewing, Vandenbelt, and Kamm.† The absorption spectrum of a vitamin obtained from biological sources and dissolved in hexane is shown in Fig. 28*a*. Several different pure organic compounds suspected of being the effective vitamins were then examined in the same spectrograph, but only the compound 2,3-dimethyl-1,4-naphthoquinone gave a spectrum closely resembling that of the vitamin. The similarity of the spectrum of this compound, shown in Fig. 28*b*, to that of the vitamin was instrumental in showing that this compound is the vitamin K_1. Then biological tests proved that this deduction was correct. The curves in Fig. 28*a* and *b* are given as extinction coefficients E at different wave

* Zcheile, *J. Phys. Chem.*, **38**, 95 (1934).

† Ewing, Vandenbelt, and Kamm, *J. Biol. Chem.*, **131**, 345 (1939).

lengths in angstroms, using a 1 per cent solution in hexane in a cell 1 cm thick. The smaller absorption in Fig. 28*a* shows that the vitamin was not completely pure or that the molecular weights were different.

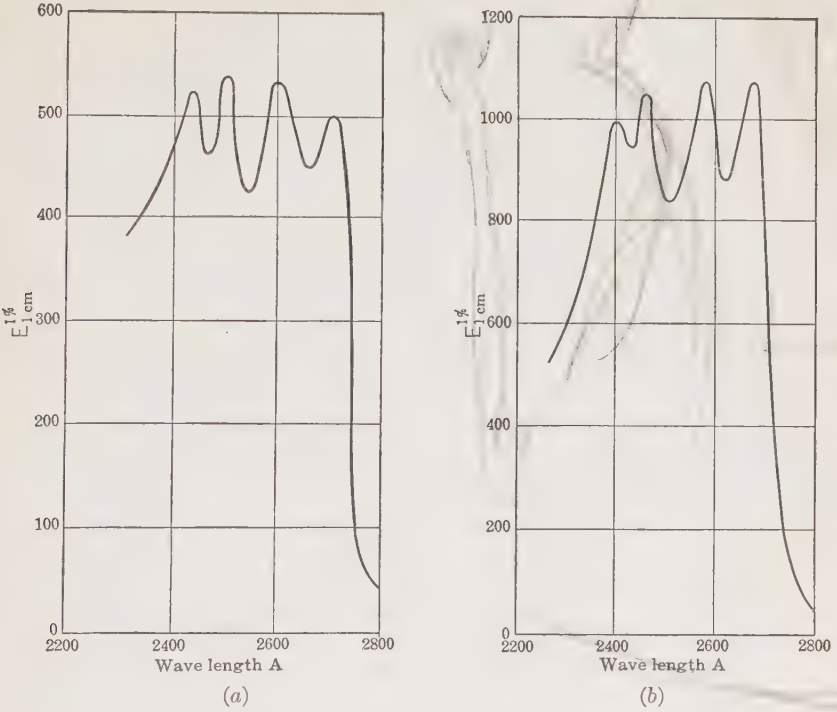


FIG. 28. Absorption spectrum (*a*) of vitamin K_1 obtained from biological sources compared with absorption spectrum (*b*) of 2,3-dimethyl-1,4 naphthoquinone.

The Parachor. It has been shown that the refraction, rotation, and absorption of light are easily measurable quantities which are useful in deciding questions of molecular structure. The determination of density may be used also. The molar volumes of organic liquids at their critical temperatures, that is, at the temperature at which the liquid is indistinguishable from the corresponding gas at high pressures, as explained on page 12, should offer possibilities for significant comparison. When the gram-molecular weights of different substances are taken, it is clear that the comparison involves equal numbers of molecules. It has been found that the volume of atoms and groups of atoms in organic compounds at the boiling point can be approximated by taking the sum of the atomic volumes. There is some theoretical basis for this relation, because it is shown on page 182 that the boiling temperatures of nonpolar liquids are roughly equal fractions of the critical temperatures.

Much more accurate results are obtained, however, if the molar volumes are compared not at their boiling points under atmospheric pressures but at temperatures at which the liquids have the same surface tension. Sugden * developed a relationship which he based partly on the observation that when the surface tensions are equal some of the differences in specific properties of different liquids tend to disappear and partly on a relation pointed out by McLeod that the surface tensions of many liquids are proportional to the fourth power of the difference between the densities of the liquid and the vapor. According to this relation, the molar parachor P of Sugden is defined as follows,

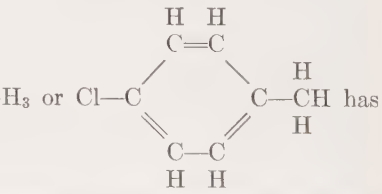
$$P = \frac{M}{D - d}\gamma^{1/4} \tag{10}$$

where γ is the surface tension defined on page 184, M is the molecular weight, D is the density of the liquid, and d is the density of the saturated vapor, all measured at the same temperature. The density of the vapor may be neglected when the vapor pressure is low. The molar parachor P is the sum of the atomic parachors, just as the molar refraction is equal to the sum of the atomic refractions, and the values for the atomic values are obtained in a similar manner by averaging many different molar values and taking differences. In the molar parachors the structural features play a part so that the physical measurements can be used in helping to decide questions of molecular structure. A summary of the values is given in Table IV.

TABLE IV

ATOMIC AND STRUCTURAL PARACHORS

C	4.8	Br	68.0	Double bond	23.2
H	17.1	I	91.0	Triple bond	46.6
O	20.0	N	12.5	5-membered ring	8.5
Cl	54.3	S	48.2	6-membered ring	6.1

Example 5. Parachlorotoluene $ClC_6H_4CH_3$ or  has a surface tension of 32.24 dynes per centimeter at 25°. Its density at this temperature is 1.065.

* Sugden, *J. Chem. Soc.*, **125**, 1177 (1924); "The Parachor and Valency," George Routledge and Sons, London, 1930.

Neglecting the density of the vapor at this temperature, what is the value of the parachor?

$$P = \frac{M}{D - d}\gamma^{1/4} = \frac{126.5}{1.065}(32.24)^{1/4} = 283$$

What is the value calculated from the atomic and structural parachors?

$$P_{\text{calc.}} = 54.3 + (7 \times 4.8) + (7 \times 17.1) + (3 \times 23.2) + (1 \times 6.1) = 283.3$$

The parachor seems to give quite accurate results in correlating structure with the physical properties of organic compounds.*

Electron Diffraction.† The arrangements of building units within crystals have been clearly revealed by means of the diffraction of X rays, as already described. A beam of electrons generated in a vacuum between two charged plates (as in a radio tube) has many of the properties of a beam of light of very short wave length (page 590). These electrons, when moving at high uniform velocities, are deflected by the nuclei of atoms, and the extent of the deflections permits a calculation of the arrangement of atoms and the distance between the atomic nuclei. Space models are constructed which account for the observed deflections in a manner similar to that by which space models are constructed for interpreting the Laue photographs obtained from the diffraction of X rays. More direct methods of interpretation are also available.‡

The X rays are very penetrating; the electron beams at lower voltages are but slightly penetrating. The X rays, then, are suitable for studying the structure of crystals and solids and liquids, but the electron diffraction is more suitable for studying gases and adsorbed gases and surface layers. The arrangement of atoms and ions in the crystals determines the crystal lattice, whereas the arrangement and distance of atoms in the individual molecules of a material in the gas phase give the molecular structure. This determination of the distance and angles between atoms in a molecule is now finding important applications in the calculation of chemical equilibria and reaction rates and in many other fields.

In carrying out measurements on molecular structure the electrons at a very uniform voltage of 40,000 volts per cm in a vacuum are shot out of a small pinhole at a photographic plate about 10 cm away. A stream of vapor of the substance to be studied is passed at a low pressure (10^{-5} mm) across this space. Short exposures of about a second

* Quayle, Owen, and Estes, *J. Am. Chem. Soc.*, **60**, 2716 (1938); also later papers.

† Brockway, *Rev. Modern Phys.*, **8**, 231–266 (1936); Clark and Wolthuis, *J. Chem. Education*, **15**, 64–74 (1938); Pirenne, "The Diffraction of X-Rays and Electrons by Free Molecules," Cambridge University Press, Cambridge, 1946.

‡ Pauling and Brockway, *J. Am. Chem. Soc.*, **57**, 2684 (1935).

each and subsequent development of the plate give rings of varying intensity, depending on the positions of atoms within the molecule. The diameters of the rings of different intensities are measured and used to decide which of many possible spatial arrangements of the atoms is the correct one.

Figure 29 is reproduced from an electron-diffraction photograph of hexamethylbenzene prepared by Dr. A. J. Stosick at the Gates Chemical Laboratory of the California Institute of Technology.

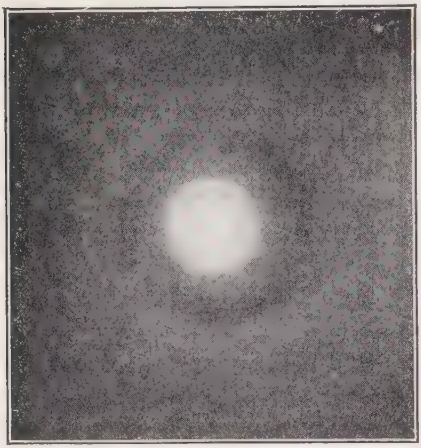


FIG. 29. Electron diffraction pattern of hexamethylbenzene.

One other example of the use of these diffraction patterns in molecular structure may be cited. Chemical evidence shows that in 1,2-dichloroethylene the two carbon atoms are joined by a double bond with one hydrogen and one chlorine atom attached to each carbon. If it is assumed that all the atoms lie in a plane, there are two possibilities: in the *cis* form the two chlorine atoms lie on the same side of the carbon double bond; and in the *trans* form they lie on opposite sides. The distances between the two chlorine atoms will be different in the two forms. Electron diffraction patterns show that in the *cis* isomer of dichloroethylene the distance is 3.22 A, and in the *trans* isomer it is 4.27 A. Models of these two molecules are shown in Fig. 34 on page 94, and the radii of some of the common elements of organic chemistry as determined by electron diffraction are given in Table VI on page 92.

Dipole Moments. Nonpolar or electrically symmetrical molecules tend to give nearly perfect gases or ideal solutions, with properties which are proportional to the number of molecules present. The simple laws of physical chemistry involving surface tensions, heats of vaporization and solution, additive volumes, and other phenomena apply much better to the nonpolar substances than to the polar. Thus, polar or electrically dissymmetrical molecules form gases which are not ideal and liquids which are associated.

Molecules are composed of positively and negatively charged particles in such numbers that they are neutral as a whole. In polar molecules there is a finite distance of separation between what may be termed the centers of gravity of the positive and negative electricity,

and the polarity of a molecule becomes less as these centers of gravity in a molecule approach each other. When placed in an electric field a polar molecule will tend to orient itself in such a way that the positive part of the molecule points toward the negative electrode and the negative part points to the positive electrode. The force required to orient the molecule will depend on the magnitude of the charges and on the distance between them. The *dipole moment* μ is described as the product of the electric charge and the distance between the two average centers of positive and negative electricity. It serves as a useful quantitative measure of the extent to which a molecule is polar.

Experimental measurements of this dipole moment have become of great importance in studying the structure of molecules, because they measure the electrical dissymmetry in molecules. Thus, they provide information concerning the shape of a molecule. Moreover, solubility and the properties of solutions, the deviations from simple gas laws and ideal solutions, and the influence of solvents on reaction rates and equilibrium constants probably can be interpreted more quantitatively through measurements of dipole moments.

The measurement of the dipole moment is complicated by the fact that all molecules, whether polar or nonpolar, possess the property of becoming polarized when placed in an electric field. Even those nonpolar molecules whose electric charges are uniformly distributed, as in H_2 or CCl_4, acquire a positive charge at the part which is nearest the negative electrode and a negative charge at the part which is closest to the positive electrode. This induced molar polarization is sometimes called distortion polarization P_D, whereas the other, permanent polarization is called orientation polarization P_μ. The latter quantity is the more significant in physical chemistry. It can be determined from measurements of dielectric constants in two different ways—by determining the dielectric constant in the gaseous state at several temperatures, or by determining the extent to which the substance in the dissolved state in a solution of a nonpolar solvent contributes to the dielectric constant of the solution. By extrapolating the measurements of dielectric constant to infinite dilution, a value is obtained which corresponds to a situation in which the molecules of solute are so far apart that they do not induce electric charges in each other. The first method is more accurate and simple in theoretical treatment but less convenient in experimental procedure. The quantitative relations follow.

The *dielectric constant* ϵ measures the relative effect of the medium on the force with which two oppositely charged plates attract each other. The dielectric constant of a vacuum is taken as unity, but for practical purposes the dielectric constant of air is nearly unity. The

dielectric constant of a liquid or gas is determined * readily by measuring the electric capacitance of a capacitor when empty and when filled. The force attracting the two plates of the capacitor depends on the size of the plates, the distance between the plates, the medium between them, and the quantity of electricity which they hold. In the same capacitor the size and distance of the plates are constant, and the ratio of forces, that is, the dielectric constant ϵ, is equal to the ratio of charges of electricity. Then,

$$\epsilon = \frac{C_x}{C_{\text{air}}} \tag{11}$$

where C_x and C_{air} refer to the electric capacitances of the capacitor when filled with the medium being measured and with air.

The molar polarization P of a substance can be calculated from its experimentally measured dielectric constant ϵ using a formula developed by Clausius and Mosotti on the basis of theories of electric charges induced by charge plates. This formula may be taken as a definition of P, thus,

$$P = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{M}{d} \tag{12}$$

where M is the molecular weight and d is the density. It may be noted that, inasmuch as ϵ is merely a ratio without physical dimensions, the molar polarization has the dimensions of molar volume, M/d.

The total molar polarization is due to two effects as already explained, thus:

$$P = P_{\text{D}} + P_{\mu} \tag{13}$$

Debye showed how these two quantities can be separated. The induced polarization P_{D}, produced by the electric fields, is unaffected by an increase in temperature, but the permanent or orientation polarization P_{μ} depends on temperature, because the random thermal agitation tends to break up the alignment of the molecules, and at the higher temperatures more of the permanent dipoles which would tend to orient themselves with respect to each other are torn apart.

It has been shown by Debye † that the permanent dipole moment μ is related to the permanent or orientation polarization P_{μ} by the formula,

$$P_{\mu} = \left(\frac{4}{3}\pi N\right)\frac{\mu^2}{3kT} \tag{14}$$

* "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1941, Chapters XIII and XXV.

† Debye, "Polar Molecules," Chemical Catalog Co., New York, 1929; or Dover Publications, Inc., New York.

where N is the Avogadro constant 6.02×10^{23}, and k is the Boltzmann constant or gas constant per molecule. The molecular gas constant is related to the molar gas constant by the equation,

$$k = \frac{R}{N} = \frac{8.314 \times 10^7}{6.02 \times 10^{23}} = 1.38 \times 10^{-16} \text{ erg per degree}$$

The factor $\frac{4}{3}\pi N$ is used in electrodynamics to convert these molecular quantities into molar quantities.

The induced polarization produced by the electric field is proportional to the polarizability or the electric moment per molecule α, induced by an electric field of unit strength. Then,

$$P_D = (\tfrac{4}{3}\pi N)\alpha \tag{15}$$

Substituting the values of P_D and P_μ just developed into equation 13 gives

$$P = P_D + P_\mu = \left(\frac{4}{3}\pi N\right)\alpha + \left(\frac{4}{3}\pi N\right)\frac{\mu^2}{3kT} \tag{16}$$

In the gaseous state the molecules are so far apart that they do not induce electric effects in adjacent molecules, and α as well as μ may be considered constants. Then equation 16 gives a straight line, thus,

$$P = a + b\frac{1}{T} \tag{17}$$

where a and b are constants.

The dielectric constants ϵ and the densities are obtained at several temperatures, and the corresponding total molar polarizations P are calculated with the help of equation 12. These values of P are then plotted against $1/T$, and the slope b of the resulting line described by equation 17 enables one to calculate the dipole moment μ, since $b = 4\pi N\mu^2/9k$. Thus:

$$\mu = \sqrt{\frac{9kb}{4\pi N}} = 0.01282 \times 10^{-18}\sqrt{b} \tag{18}$$

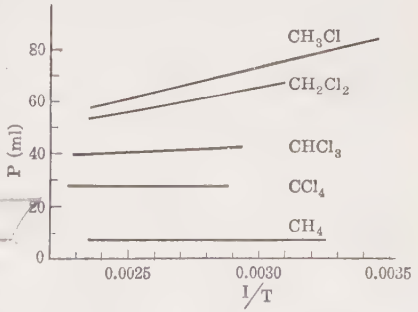


FIG. 30. Calculation of dipole moments of gases from molar polarizations at different temperatures.

These calculations are illustrated in **Fig. 30** for the chlorine-substituted compounds of methane as measured by Sänger.* It is seen that CH_4 and CCl_4 give horizontal lines

* Sänger, *Physik Z.*, **27**, 562 (1926).

when P is plotted against $1/T$. The slope is zero, and the dipole moment is zero. This is to be expected because the molecules are symmetrical. The sloping lines for $CHCl_3$, CH_2Cl_2, and CH_3Cl show that the molecules have dipole moments owing to the unsymmetrical arrangement of the negative chlorine atoms. The steeper the slope the greater is the dipole moment.

According to the second method for the determination of μ, already mentioned, the dipole moment μ can be determined by extrapolating the molar polarization P of the solutions to infinite dilution, all the measurements being made at constant temperature. The close relation which exists between dielectric constant ϵ and refractive index n, when the molecules are far apart, leads to the following equation at infinite dilution:

$$P_D = \frac{n^2 - 1}{n^2 + 2}\frac{M}{d}$$

Then, the permanent molar polarization P_μ of the solute can be obtained from the measured molar polarization P_∞ at infinite dilution and the known refractive index of the solute, thus:

$$P_\mu = P_\infty - \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d} \tag{19}$$

Once P_μ has been determined, the value of μ can be determined from equation 14 as follows:

$$\mu = 0.01282 \times 10^{-18} \sqrt{P_\mu T}$$

Dipole moments of several typical substances are given in Table V. The dipole moment is always of the order of 10^{-18} electrostatic units.

TABLE V

DIPOLE MOMENTS

In Electrostatic Units

$AgClO_4$	4.7×10^{-18}	C_6H_5Cl	1.73	HCl	1.03
$C_6H_5NO_2$	4.23	C_6H_5OH	1.70	HBr	0.79
$(CH_3)_2CO$	2.8	C_2H_5OH	1.70	HI	0.30
H_2O	1.84	$C_6H_5NH_2$	1.56	N_2O	0.14
CH_4	0	NH_3	1.46	CO	0.12
CH_3Cl	1.86	H_2S	1.10	CS_2	0
CH_2Cl_2	1.59	H_2	0	C_2H_4	0
$CHCl_3$	1.15	Cl_2	0	C_2H_6	0
CCl_4	0	CO_2	0	C_6H_6	0

This is to be expected, because the unitary charge of electricity is 4.8×10^{-10} electrostatic unit (page 396), and the diameter of most molecules is of the order of 10^{-8} cm. The dipole moment is the product of the charge and the distance between the two charges. Dipole moments are sometimes expressed in Debye units, one such unit being 10^{-18} electrostatic unit.

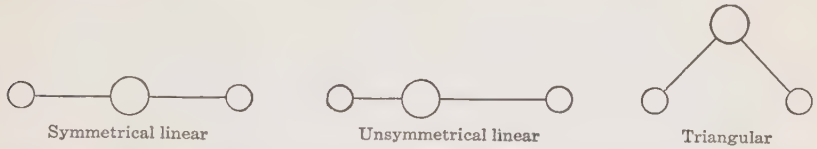


FIG. 31. Possible structures of carbon dioxide. The symmetrical line model is the only one consistent with the observed dipole moment of carbon dioxide.

Carbon dioxide and water might have structures corresponding to a symmetrical linear molecule, to an unsymmetrical linear molecule, or to a triangle as shown in **Fig. 31.** The dipole moments recorded in Table V show that carbon dioxide has zero moment and the molecule must be symmetrical and linear. If it were unsymmetrical or triangular there would be an unbalancing of the electric charges. On the other hand, water has a pronounced dipole moment and it cannot have the symmetrical linear structure. Measurements of band spectra show that it has the triangular form rather than the unsymmetrical linear form.

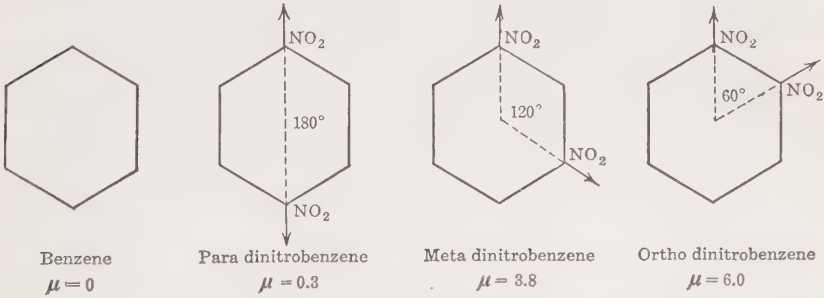


FIG. 32. Dipole moments of the dinitrobenzenes.

To a certain extent dipole moments of groups of atoms may be added as vectors in molecules, but there are deviations which are important aids in determining the molecular structure.*

* Additional examples of the use of dipole moments are given by Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931; Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933, pages 138–198.

The *cis* and *trans* isomers of dichloroethylene have been discussed already in connection with electron diffraction. Measurements of dipole moments are also significant. The *cis* isomer with the two chlorines on one side of the carbon–carbon double bond has a dipole moment of 1.56×10^{-18}, whereas the more symmetrical *trans* isomer has a dipole moment of only 0.3×10^{-18}.

The disubstituted benzenes, shown in **Fig. 32,** are interesting. The arrows indicate the vectors and show that the dipole moment increases progressively as the molecule becomes more unsymmetrical.

Atomic Models. The distance between atoms may be determined from measurements of electron diffraction. The "bond angles" which valence bonds make inside the molecule may be found from measurements of dipole moments. These considerations apply best to the nonpolar compounds or covalent molecules in which atoms are held together chiefly by electron pairs rather than by electrostatic attraction.

By measuring the interatomic distances in many nonpolar compounds Pauling has been able to assign bond lengths or atomic radii to each element on the assumption that these bond lengths are additive. Not only is the atomic radius fixed for a given atom, but also the bond angles are fixed. These rules hold as long as the bonds are normal and the molecule is free from strain. Table VI gives the bond radii for a number of atomic species.

The single bond of carbon has a bonding radius of 0.77 A, and hydrogen has a bonding radius of 0.30 A, and so the separation for C—H is $0.30 + 0.77 = 1.07$ A. Similarly, the interatomic distance for C—C is $0.77 + 0.77 = 1.54$ A. When double bonds are present, all the adjacent bonds lie in a single plane. Thus ethylene and benzene have planar structures.

TABLE VI

Bond Radii

(angstroms)

Hydrogen	0.30	Nitrogen (nitrate) (single)	0.70
Carbon (single bond)	0.77	Chlorine	0.99
Carbon (double bond)	0.67	Bromine	1.14
Carbon (triple bond)	0.60	Iodine	1.33
Oxygen (single bond)	0.66	Nitrogen (cyanide)	0.55
Oxygen (double bond)	0.57	Carbon (benzene) (C—C)	0.69
Nitrogen (amino)	0.70	Carbon (benzene) (C—H)	0.77
Nitrogen (nitrate) (double)	0.65		

These bond radii and bond angles are represented in **Fig. 33.** Models are available * in which nearly 1 cm represents 1 A, and the faces of

* Fisher-Hirschfelder atomic models.

the atoms are cut so as to give the correct bond angles. Models of molecules may then be built up which represent the actual relations on a large scale, and certain deductions can be drawn from these models. Models are shown in Fig. 33 for hydrocyanic acid, ethanol, and benzene.

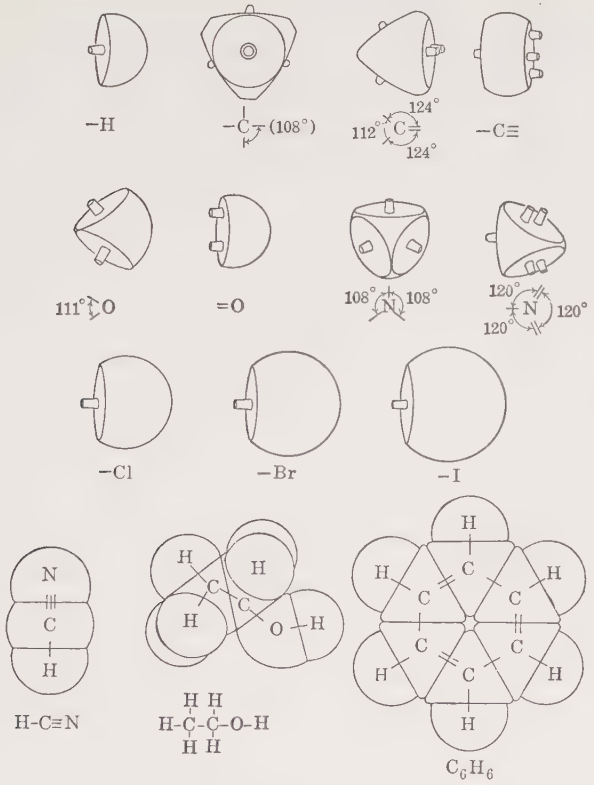


Fig. 33. Atomic and molecular models giving correct interatomic distances and angles.

In **Fig. 34** the *cis* and *trans* forms of dichloroethylene are shown, and the reasons for the difference in dipole moments is readily apparent.

Hexane, which is shown also in Fig. 34, has a long snakelike structure which can move around in various positions, but the probabilities of free motions of the cyclohexane shown just below it are greatly reduced. This reduction of the probable motions leads to a decrease in entropy, which is discussed on page 144.

Whenever the interatomic distance is not equal to the sum of the bond radii, it may be concluded that there is something abnormal, such as a strained position or the existence of more than one molecular

structure, brought about by rapid oscillation of the electrons between different positions, as described on page 38. Conjugated double bonds

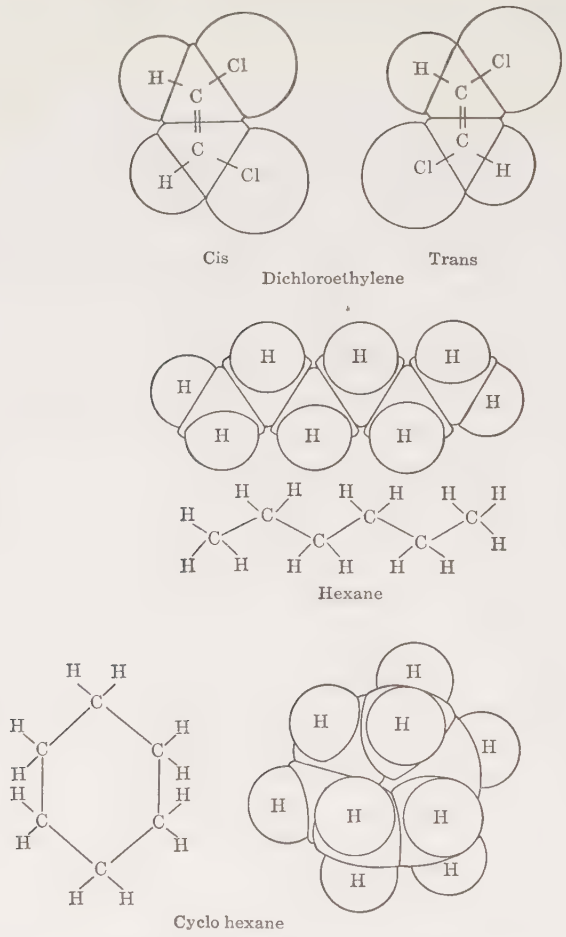


FIG. 34. Typical molecular models.

are good examples of such resonating structures. Butadiene, for example, has the structure,

$$-C=C-C=C-$$

and illustrates this type of resonance. It is found that in butadiene the carbon–carbon distances are not exactly equal to the sum of the normal bond radii. When resonance occurs, the compounds are more stable than would otherwise be expected, and they have abnormally

low heats of reaction; that is, an extra amount of energy is required to pull the atoms apart when new compounds are formed.

Summary of Experimental Methods. We have seen that there are several different ways in which we can obtain information regarding the arrangements of atoms within a molecule. It is possible to choose between different structural features by finding the proper atomic properties which will add up to give the experimentally determined molar property. Molar volumes based on density, parachors involving surface tension, and molar refractions calculated from the refraction of light are examples which have been discussed.

Optical rotation is useful sometimes in showing that the molecule contains an asymmetric carbon atom. Determination of the dipole moment gives information concerning the shape of the molecules and the bond angles, whereas the determination of the magnetic moment permits conclusions regarding the type of electron binding.

Electron diffraction and X-ray patterns give information from which the atomic spacings can be determined through construction of models which will reproduce the observed effects.

It is shown later that calorimetric measurements of the heats of reaction of a series of compounds sometimes bring out abnormalities which can be explained on the basis of special features in the molecular structure.

Finally, the information obtained from absorption-band spectra, in the visible, ultraviolet, and infrared, and the Raman spectra, as discussed in Chapters XIX and XX enables one to calculate vibration frequencies and force constants of the atoms within the molecule. These aspects of the molecular structure are important in determining thermodynamic quantities.

REFERENCES

Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, 1946, Chapter VIII.

Brode, "Chemical Spectroscopy," John Wiley & Sons, New York, 1939.

Gilman, "Organic Chemistry," John Wiley & Sons, New York, 1943, Chapters 20 and 21.

Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931.

Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

Selwood, "Magnetochemistry," Interscience Publishers, New York, 1943.

Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, New York, 1946.

PROBLEMS

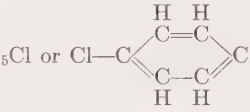
1. Calculate the molar refraction of diethyl ether, $(C_2H_5)_2O$. The refractive index, n_D at 17.1° is 1.35424, and the density at 17.1° is 0.7183 g per milliliter. Compare this value with the sum of the atomic refractions.

Ans. (*a*) 22.43. (*b*) 22.32.

2. Geraniol has the formula $C_{10}H_{18}O$, and its chemical behavior is such as to warrant the conclusion that it is a primary alcohol. The value of n_D is 1.4745 from which the molecular refraction is calculated to be 48.71. What conclusions can you draw regarding the structure of this compound? *Ans.* Two double bonds.

3. The specific rotation α_D of a solution of *d*-ethoxysuccinic acid in water is 33.02 at 17° C. Calculate the concentration of this compound in grams per liter in a solution which has a rotation of 2.02° when measured in a polarimeter at 17° C in which the container of the solution is 20 cm long. *Ans.* 30.6 g per liter.

4. Using Beer's law and Lambert's law, derive the formula for the use of the colorimeter, $c_x = \frac{d_s}{d_x} c_s$, where c and d stand for the concentrations and depths, s refers to the standard solution, and x refers to the unknown solution.

5. Chlorobenzene C_6H_5Cl or  has a surface tension of 33.19 dynes per centimeter at 25°. Its density at this temperature is 1.106.

(*a*) If the density of the vapor at this temperature is neglected, what is the value of the parachor?

(*b*) What is the value calculated from the atomic and structural parachors?

Ans. (*a*) 244.1. (*b*) 244.3.

6. The dielectric constants and densities of germanium tetrachloride at various temperatures are tabulated. Calculate the molar polarizations at these temperatures, and determine the dipole moment. *Ans.* Zero.

$t°$	0	20	30	40	50
ϵ	2.491	2.443	2.417	2.395	2.370
d	1.9226	1.8762	1.8533	1.8296	1.8063

7. By extrapolation the molar polarization of pyridine oxide, C_5H_5NO, in an infinitely dilute solution in dioxane is found to be 411 at 25°. The molar refraction of C_5H_5NO is 28 and this is approximately equal to P_D. Calculate the dipole moment.

Ans. 4.33×10^{-18}.

---

8. Calculate from the atomic refractions the refractive index of allyl acetate, n_D, at 20°. The density of allyl acetate at 20° is 0.9276. The formula is $CH_3COOCH_2CH{=}CH_2$. The experimental value is 1.4045.

9. A solution of *l*-mandelic acid in water containing 1.56 g in 100 ml rotated polarized light 4.91° in a polarimeter which had a cell 20 cm long. The D line of sodium was used as a light source. Calculate the specific rotation.

10. At 35° the surface tension of butyl laurate ($C_{11}H_{23}COOC_4H_9$) is 27.47 dynes per centimeter. The density is 0.8490. Calculate the parachor of the compound, assuming that the density of the vapor is negligible, and compare it with the value calculated from the atomic parachors.

11. Calculate what concentration of bromine in a layer 5 cm thick will be necessary to absorb 50 per cent of the blue light passing through it.

12. (*a*) With the help of Fig. 26, plot the logarithm of the per cent of light transmitted at 5400 A against the concentration of iron expressed in parts per million.

(*b*) Green light of 5400 A is passed through a solution containing a trace of iron to which dioxime has been added. One centimeter of the resulting colored solution absorbs 50 per cent incident light. What was the concentration of iron expressed in parts per million?

13. The following data for a sample of linseed oil at 25° were found experimentally: Refractive index $n_D = 1.4792$; density = 0.9260; molecular weight $M = 783$ (polymerized); dielectric constant $\epsilon = 2.349$ extrapolated to infinite dilution in benzene. Calculate the dipole moment of the linseed oil at 25°.

14. The molar polarization of silicobromoform $SiHBr_3$ is 46 at 25°. The induced electrical moment α may be taken as 1.308×10^{-23}. Calculate the dipole moment of this molecule.

---

15. The refractive index of *n*-heptyl fluoride $CH_3(CH_2)_5CH_2F$ is 1.3861 at 20°, and the density is 0.804.

What is the refractive index of fluorotrichlormethane CCl_3F at 20° if the density is 1.494?

16. A preparation of *l*-proline when dissolved in water gave a concentration of 23 g per liter at 20° and rotated polarized light from the D line of sodium through −3.05°, as measured with a polarimeter in a cell 20 cm long. The specific rotation at 20° of pure *l*-proline is −84.9°. What conclusions can be drawn as to the purity of the product if it is assumed that any impurities are optically inactive?

17. Ethylene dibromide $CH_2Br—CH_2Br$ at 25° has a density of 2.170 and a surface tension of 38.2. Calculate the parachor, and compare it with the sum of the atomic parachors.

18. At 30°, the density of boron triethyl $B(C_2H_5)_3$ is 0.6774, and its surface tension is 19.84 dynes per centimeter. Using the atomic parachors of carbon and hydrogen, calculate the atomic parachor of boron.

19. In order to test the validity of Beer's law in the determination of vitamin A, solutions of known concentration were prepared and treated by a standard procedure with antimony trichloride in chloroform to produce a blue color. The per cent transmission of the incident filtered light for each concentration in a given cell is as follows:

Conc. (micrograms per milliliter)	*Per Cent Transmission*
1.0	66.8
2.0	44.7
3.0	29.2
4.0	19.9
5.0	13.3

Plot these data so as to give a straight line. A solution, when treated in the standard manner with antimony chloride, transmitted 35 per cent of the incident light in the same cell. What was the concentration of vitamin A in the solution?

20. A certain solution of a blue dye absorbs 25 per cent of the red light in a thickness of 1 cm.

(*a*) How much of the light will be absorbed by 2 cm of solution?

(*b*) How much will be absorbed by 10 cm of solution?

(*c*) What depth of solution will be required to absorb only 10 per cent of the light?

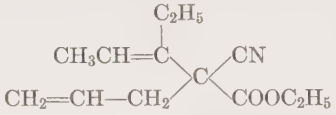
21. The molar polarization P of ammonia varies with temperature as follows:

t (°C)	19.1	35.9	59.9	113.9	139.9	172.9
P (ml)	57.57	55.01	51.22	44.99	42.51	39.59

(*a*) Plot P against $1/T$, and determine the dipole moment of ammonia.

(*b*) If the density of ammonia gas at 59.9° and 1 atm is 0.632 g per liter (0.000632 g per milliliter), what is the dielectric constant of ammonia under these conditions?

22. In synthesizing ethyl (*l*-ethyl propenyl) allylcyanoacetate,



none of whose physical constants were known, a product was obtained having a refractive index n_D^{25} of 1.4617 and a density of 0.9704 at 25°. What conclusions can be drawn as to the purity of the compound?

23. Nicotine is examined in a tube 10 cm long, at 25° with the sodium D line. $[\alpha]_D^{25} = -162°$; $d_{25} = 1.009$. Calculate the percentage of error in the value of $[\alpha]$ caused by (*a*) an error of 0.1° in the angle, (*b*) an error of 0.1 mm in tube length, and (*c*) an error of 0.01 in density.

CHAPTER VI

HEAT, WORK, AND HEAT CAPACITY

Thermodynamics. The quantitative relations between heat and other forms of energy are studied in the science of thermodynamics. They are important because all other forms of energy tend to change into heat, and the quantitative measure of this tendency is useful in predicting physical-chemical behavior.

Thermodynamics has been used in physics for a century, and it has found extensive applications in engineering; but its practical application in chemistry is a considerably later development. The present chapter provides an introduction to the simple concepts of heat and work. It is followed by a chapter on heat measurements in chemical reactions and then by a chapter on the more abstract concepts of thermodynamics. Throughout the study of solutions and chemical equilibria, these concepts will be applied to correlate and explain the observed facts. More detailed studies of solutions of electrolytes are given in Chapter XVII.

Forms of Energy. Energy can be made to do work. A force of 1 dyne is that force which gives to a mass of 1 g an acceleration of 1 cm per second per second. The unit of energy is the erg, which is the energy produced by a force of 1 dyne acting through a distance of 1 cm. A larger unit, the joule, which is equal to 10^7 ergs, is a more convenient unit.

Energy may be stored in a given system by virtue of position, as, for example, a stone above the earth's surface, or a spring under compression; or by virtue of chemical properties due to the arrangement of atoms and electrons within a molecule. Energy may also exist in other forms, such as the kinetic energy of a moving ball or molecule.

This energy may be released, under the proper conditions, to do work: to push a piston in an engine cylinder or to send a current of electricity through the windings of an electric motor. The energy may be converted into heat, thus raising the temperature of the system itself or of the surroundings. Energy, work, and heat are all expressed in the same units: calories, joules, or ergs.

Although symbols are employed to represent the total energy stored in a system, it should be borne in mind that usually it is not necessary to know this energy in absolute terms.

Generally, we are concerned only with the change in energy which takes place during the operation which we are studying. For example, in the burning of coal we are interested in the energy released by changing the carbon and oxygen into carbon dioxide, and we are not often concerned with the energy that may still reside in carbon dioxide by virtue of its temperature above absolute zero, or by virtue of the arrangement of the atoms and electrons within the molecule, or by the stability of the nuclei of the atoms. Again, we calculate that the energy required to lift a kilogram weight through 10 centimeters against the force of gravity * is

$$1000 \text{ g} \times 980.7 \text{ cm/sec}^2 \times 10 \text{ cm} = 9.807 \text{ million ergs}$$

and that after the lifting operation, the weight possesses 9.807 million ergs of energy more than it had before. We are not concerned with the energy which the weight possesses by virtue of its distance from the center of the earth.

When the weight just referred to falls back to its original level, the potential energy of position is converted into kinetic energy of motion, and, when it is stopped by collision with the ground, this kinetic energy is converted into heat energy.

Energy may be expressed as the product of two factors—an intensity factor and a capacity factor. Examples are given in Table I.

TABLE I

Intensity and Capacity Factors of Energy Involved in Various Processes

Energy	Intensity	Capacity
Mechanical (ergs)	Force (dynes)	Change in distance (cm)
Surface (ergs)	Surface tension (dynes per cm)	Change in area (sq cm)
Volume expansion (ergs)	Pressure (dynes per sq cm)	Change in volume (cm^3)
Heat (calories)	Difference in temperature (degrees)	Heat capacity (calories per degree)
Electric (joules)	Difference in potential (volts)	Coulombs (amperes × seconds)

It is evident that the different energies may be compared but that no relation exists between the intensity factors alone or between the capacity factors alone. For example, electric energy may be converted

* The force of gravity varies somewhat with latitude and distance above sea level and composition and density of the earth's crust but the value 980.7 dynes is used for the calculations of this book.

quantitatively into heat energy, but the rise in temperature cannot be calculated from the voltage unless the number of coulombs and the heat capacity of the system are known. It is clear also that the same quantity of work may be accomplished by a small quantity of water passing through a turbine from a great height as from a large quantity of water falling through a short distance.

The First Law of Thermodynamics. According to the first law of thermodynamics, *the sum of all the energies in an isolated system is constant.* In other words, energy may be transformed from one form into another, but it cannot be created or destroyed. This law was formulated in 1842 by Mayer following the experiments of Joule and Helmholtz on the transformation of heat into work. Many exact experiments have since shown that mechanical or electrical work can be transformed completely into heat. In some of these experiments a measured amount of work was used in stirring a liquid while the rise in temperature was measured, and in others a known quantity of electricity was passed through a heating coil of known resistance immersed in a liquid containing a thermometer.

Heat is expressed in ergs or joules or, more commonly, in calories. The 15° calorie (that is, the heat required to raise one gram of water from 14.5° to 15.5°) is equivalent to 4.1855 absolute joules. For several years American physical chemists have defined the "calorie" arbitrarily as equal to 4.1833 international joules, a value which is now accepted as 4.1840 absolute joules.* This definition of the calorie is used throughout this book. A table of physical-chemical constants and their best values is given on page 699.

Our confidence in the first law of thermodynamics rests largely on the fact that no exceptions to it have yet been found. At first sight one might think that the energy expended in lifting a piece of iron is destroyed if the iron is dissolved in sulfuric acid, but the iron in the resulting ferrous sulfate is at a higher level and possesses potential energy equal to the energy expended in the lifting. If energy is expended in coiling a steel spring and the spring is dissolved in acid, the energy appears to be lost; but more heat is evolved by a coiled spring than by an uncoiled spring. The energy is immediately distributed throughout all the molecules of the solution. The difference is so small, however, that it has not been detected by present calorimetric methods.

Even the new developments in nuclear reactions do not contradict

* The United States Bureau of Standards, effective Jan. 1, 1948, has adopted the value 1 international joule = 1.000165 absolute joules, in agreement with many countries of the world as recommended by the International Committee on Weights and Measures. *Circ. Natl. Bur. Standards* C 459.

the first law; for, according to the theory of relativity, energy possesses mass, and the large evolution of energy produced by reactions between atomic nuclei in transmutation experiments (page 655) is offset by the actual decrease in mass. Einstein showed that

$$1 \text{ g} = 9 \times 10^{20} \text{ ergs} \tag{1}$$

The proportionality factor 9×10^{20} is the square of the velocity of light expressed in centimeters per second. It is evident that the law of the conservation of energy and the law of the conservation of mass are essentially the same and that no violation of thermodynamics occurs when matter is converted into energy, or energy into matter. However, nuclear transformations and changes in total mass are not involved in ordinary chemical and physical phenomena, and their discussion is reserved for Chapter XXI. Equation 1 is of no importance in most physical-chemical phenomena.

A change in the energy of a system will be brought about if the system gives or receives work, or if it absorbs or evolves heat. The *work* is designated by w. A positive sign indicates that the work is done by the system on its surroundings and a negative sign shows that the system is having work done on it, as, for example, when a gas is compressed by the applications of external pressure. The *heat* exchange is designated by q; $+q$ for heat absorbed by the system and $-q$ for heat evolved.

In *chemical* thermodynamics we are not ordinarily interested in the energy which a system has by virtue of its distance from the center of the earth or by virtue of any movement of the system through space. We are interested in the *internal energy* E, of which chemical energy is an important manifestation. It includes many complicated factors such as molecular, atomic, and electronic motions.

The symbol Δ always indicates a change, and in physical chemistry it refers to the difference between the values of a property in the initial and the final states. For example, if E_1 represents the internal energy in the initial state and E_2 the internal energy in the final state, in the reaction,

$$\text{state}_1 \rightarrow \text{state}_2$$

Then

$$\Delta E = E_2 - E_1$$

The initial state 1 is taken as the state which happens to be written down at the left of a chemical equation, and the final state 2 is designated as the state written at the right. This convention applies to any chemical or physical change.

Since energy can be neither created nor destroyed, it follows that the internal energy of the final state must be equal to the internal energy of

the initial state plus the energy added in the form of heat or any kind of work. Then,

$$E_2 = E_1 + (q - w)$$

or

$$E_2 - E_1 = \Delta E = q - w \tag{2}$$

This equation may be regarded as a mathematical formulation of the first law of thermodynamics.

It is important to realize that E_1 and E_2 are thermodynamic quantities, which are characteristic of the system as fixed. ΔE is the same, irrespective of the path followed in going from state 1 to state 2. The quantities q and w, however, can vary greatly with the experimental conditions.

If there is no change of internal energy, as in the isothermal expansion of an ideal gas, the work done must be exactly equal to the heat absorbed. Again, if there is a chemical reaction and the internal energy of the system decreases, that is, E_2 is less than E_1, the released energy may appear as heat evolved and work done. Nothing is stated regarding the relative amounts of heat and work, but the two taken together $(q - w)$ must be equal to the change in internal energy. Under special conditions it is possible to have either q or w or both equal to zero.

For infinitesimal changes, equation 2 is written

$$dE = dq - dw \tag{3}$$

but there is an important reservation which must be made regarding the use of dq and dw. Changes in internal energy E, like changes in pressure or volume, depend only on the initial and final state and are independent of the intermediate stages. Mathematically they may be classed as perfect differentials, and

$$\int_{E_1}^{E_2} dE = E_2 - E_1 = \Delta E$$

On the other hand, q and w do not represent differences between initial and final states. They refer to processes rather than states, and their values depend on the manner in which the change is carried out. The terms dq and dw are not perfect differentials, and their integrals should not be written as the differences between initial and final values (for example, as $q_2 - q_1$), but simply as q or w.

Reversible Processes. *Vaporization of a Liquid.* When a gas increases in volume, it pushes back the surrounding atmosphere and does work. Imagine that a liquid is placed in a cylinder provided with a weightless frictionless piston and that it is set into a large reservoir at the boiling point of the liquid. The fact that no machine can be built

with a weightless frictionless piston in no way affects the conclusions drawn from this idealized process. The vapor pressure of the liquid at this temperature is exactly equal to the atmospheric pressure, and the whole system is in a state of equilibrium. If now the temperature of the reservoir is raised by an infinitesimal amount, the vapor pressure of the liquid will be slightly greater, and the piston will be pushed back against the atmospheric pressure. As more liquid evaporates, the volume increases, and the pressure in the cylinder is thus maintained constant; heat flows in from the reservoir to maintain the temperature constant and offset the cooling caused by vaporization.

The work done is the product of the resisting pressure and the increase in volume. The increase in volume is the distance through which the piston is driven out multiplied by the cross-sectional area of the piston. If the liquid in the cylinder is water, the temperature will be 100°, and, when 1 mole has been evaporated, the increase in volume can be calculated on the assumption that the vapor behaves as an ideal gas and that the volume of the liquid (0.018 liter) is negligible:

$$w = p\,\Delta V = 1 \times (22.41 \times 373.1/273.1) = 30.6 \text{ liter-atm}$$

Since it is assumed that the ideal-gas laws are obeyed, RT may be substituted for $p\,\Delta V$. Then,

$$w = RT = 0.08206 \times 373.1 = 30.6 \text{ liter-atm}$$

or

$$w = RT = 1.987 \times 373.1 = 741.3 \text{ cal}$$

The work done in this process depends only on the temperature and is independent of the cross section of the piston or the pressure or volume. In very exact work it is not legitimate to consider a vapor at its boiling point as a perfect gas, and then the volume change must be measured experimentally or calculated with more exact equations of state.

The energy consumed in doing this external pressure-volume work comes from heat absorbed from the reservoir by the evaporating liquid. A great deal more energy is absorbed, however, in separating the molecules from their neighboring molecules in the liquid. To vaporize a gram of water at 373.1° K and atmospheric pressure, 539 cal is required. This corresponds to 18.02×539 or 9713 cal per mole. Then, under these conditions of constant pressure the total heat absorbed is equal to the sum of the two quantities as given by equation 4.

$$q = \Delta E + w = \Delta E + p\,\Delta v \qquad (4)$$

Since $q = 9713$ and $p\,\Delta V = 741$, the change in internal energy ΔE must be 8972 cal.

This process of absorbing heat and doing external work is reversible in the example just given, because at any time the vaporization can be stopped by decreasing the temperature by an infinitesimal amount or by increasing the pressure slightly, thus making internal and external pressures exactly equal. Increasing the pressure still further by an infinitesimal amount causes the vapor to condense and give back the heat of vaporization to the reservoir. A *reversible process*, then, is defined as one which may be reversed at will by making infinitesimal changes.

After a mole of water has been evaporated by decreasing the pressure, it can be condensed again by increasing the pressure, and thus the whole system may be restored to its original condition. Such a process, which involves a series of changes and restores the system to its original condition, is called a *cycle*. A *reversible cycle* is one which is carried out by applying infinitesimal changes under conditions such that the system is at all times practically in a state of equilibrium.

Maximum Work by Isothermal Expansion. The maximum work which can be done by the *isothermal expansion* of a perfect gas is an important quantity in theoretical chemistry. Imagine a gas enclosed in a cylinder fitted with a frictionless and weightless piston and placed in a thermostat at the temperature T. The external pressure on the piston is decreased by a small amount, $-\Delta p$, and the gas expands by an amount Δv. In this expansion the pressure of the gas in the cylinder decreases until it becomes equal to the external pressure, and then the piston ceases to rise. This process differs from the one described previously on page 102 where the gas was in contact with *liquid* at its boiling point so that the pressure in the cylinder was maintained constant. A second decrease in pressure produces a second expansion Δv, and, as the pressure is decreased in successive amounts, the volume undergoes a series of expansions. In each little expansion the work done is the external pressure multiplied by Δv, and the total work done in expanding from the *initial* volume v_1 to the *final* volume v_2 is equal to the sum of the work done in each expansion.

The maximum work is obtained when the Δv's are made infinitesimally small, and under these conditions the exact value is readily obtained by integral calculus,* thus:

$$w_{\text{max.}} = \int_{v_1}^{v_2} p \, dv \tag{5}$$

Only if the work done is maximum work, can sufficient energy be stored to reverse the process, compressing the gas and restoring the

* The significance of this equation may be found in Daniels, "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., New York, 1928, pages 162–164.

original conditions. Under the conditions of maximum work the internal pressure can be substituted for the external or resisting pressure, because the two can never differ by more than an infinitesimal amount dp, and the system is then always practically in a state of equilibrium; that is, it is a reversible process.

If 1 mole of a perfect gas is taken, $pV = RT$, or $p = RT/V$, and

$$w_{\text{max.}} = \int_{V_1}^{V_2} \frac{RT}{V}\, dV$$

Since R and T are constants, integration gives

$$w_{\text{max.}} = RT\int_{V_1}^{V_2} V^{-1}\, dV = RT \ln \frac{V_2}{V_1} = RT2.303 \log \frac{V_2}{V_1} \qquad (6)^*$$

The maximum work done by a gas in expansion is equal to the minimum work required to compress the gas, and the calculation is made by simply interchanging the limits of integration and using the smaller volume for the upper limit. In integrations, the upper limit always refers to the final state and the lower limit refers to the initial state. The signs then take care of themselves. The negative value obtained for w in compression means that work is done on the gas.

Example 1. What is the maximum work which can be obtained by the isothermal expansion of 1 mole of an ideal gas at 0° from 2.24 liters to 22.4 liters?

$$w_{\text{max.}} = 2.303RT \log \frac{V_2}{V_1} = 2.303 \times 1.987 \times 273.1 \times \log 10 = 1250 \text{ cal}$$

Then 1250 cal is also the minimum amount of work required to compress the gas from 22.4 to 2.24 liters at 0°.

The maximum work for 1 mole of gas may be calculated in terms of pressures instead of volumes since $p_1V_1 = p_2V_2$ and $V_2/V_1 = p_1/p_2$. Then,

$$w_{\text{max.}} = RT \ln \frac{p_1}{p_2} = -RT2.303 \log \frac{p_2}{p_1}$$

Absorption of Heat. In many problems the only work done is pressure–volume work, that is, $dw = p\, dv$. In the special case where there is no volume change, dv is zero and w is therefore zero. Then for proc-

* The more general equation for n moles of perfect gas is $w_{\text{max.}} = nRT2.303 \log v_2/v_1$. The capital V is used for 1 mole.

esses in which the volume is kept constant and no electric or other work is done, equation 2 can be written

$$q_v^* = \Delta E + 0 = \Delta E \tag{7}$$

In other words, the *heat of a process, measured under conditions of constant volume, is equal to the change in internal energy.* According to this equation, if no outside work is done, the heat evolved, $-q_v$, is equal to the decrease in the internal or chemical energy.

Constant-pressure processes are generally more common in chemistry than the constant-volume processes, because most operations are carried out in open vessels. It is convenient then to use another quantity which involves pressure and volume.

Enthal'py or *heat content* † is such a quantity. It is defined by the equation:

$$H = E + pv \tag{8}$$

Changes in enthalpy rather than absolute values are important in chemistry and

$$\Delta H = \Delta E + \Delta(pv) \tag{9}$$

The change in enthalpy can be visualized readily under the special condition of constant pressure as equal to the increase in internal energy plus the pressure–volume work of expansion or compression.

$$\Delta H = \Delta E + p\,\Delta v \quad \text{(at constant pressure)} \tag{10}$$

Under this condition of constant pressure equation 4 applies and

$$q_p = \Delta E + p\,\Delta v$$

Substituting the equivalent of ΔH in equation 10 gives

$$q_p = \Delta H \tag{11}$$

In other words, the *heat absorbed in a process at constant pressure is equal to the increase in enthalpy.*

Example 2. One mole of magnesium is dissolved in an excess of hydrochloric acid at 25° in (*a*) an open beaker and (*b*) a closed bomb. The heat of the

* A subscript below a quantity indicates that the property indicated by the subscript is kept constant; thus, q_v shows that the process is restricted to constant volume.

† The term heat content was used by Lewis and Randall and has been adopted in previous editions of this book. However, the term enthalpy (accented on the second syllable) is widely used by physicists and engineers, and it is gaining in usage among physical chemists so that for the sake of uniformity it seems best in this edition to call the quantity $E + pv$ *enthalpy*, rather than heat content.

reaction, at constant pressure, q_p, is $-110{,}130$ cal. What is the heat of reaction at constant volume, q_v?

$$\text{Mg} + 2\text{HCl (in water solution)} = \text{MgCl}_2 + \text{H}_2$$

$$q_p = q_v + p\,\Delta v = q_v + \Delta n\,RT$$

where Δn = the increase in the number of moles of gas = $+1$. Then

$$q_v = -110{,}130 - 1 \times 1.987 \times 298.1 = -110{,}722 \text{ cal}$$

At constant pressure the evolution of heat is less than the heat of reaction at constant volume by the amount of energy required to do the external work, of pushing out one mole of hydrogen gas against the atmospheric pressure, namely, 592 cal. It is to be noted that the final state is not the same in the two reactions, the hydrogen occupying a larger volume in the first. It is assumed that the internal energy of the products is practically independent of pressure, as shown in a later section, and that hydrogen behaves as an ideal gas.

Example 3. Show that the work done by the liberation of a mole of an ideal gas in a reaction at constant pressure and temperature is independent of the pressure of the gas and independent of the cross section of the vessel in which it is liberated. The work done is given by the relation,

$$w = p\,\Delta V$$

If the pressure is reduced to half an atmosphere, the volume will be twice as large, and the product $\frac{1}{2}p \times 2\Delta V$ will be the same. Likewise, if the cross section of the cylinder and piston is doubled, the displacement of the piston for a given evolution of gas will be halved, and ΔV will remain unchanged.

Heat Capacity. Heat can be absorbed not only by physical and chemical changes but also by simply raising the temperature. *Heat capacity* c is defined as the heat absorbed divided by the increase in temperature, when the increase is small. When the absorption of heat is carried out under a condition of constant volume, the heat capacity is given by the expression,

$$c_{v\,\text{avg.}} = \frac{q_v}{T_2 - T_1} = \frac{E_2 - E_1}{T_2 - T_1} \tag{12}$$

For small temperature differences,

$$c_v = \left(\frac{\partial E}{\partial T}\right)_v^{*} \tag{13}$$

* The partial differential ∂ (appendix, page 696) indicates that E is the only variable which changes with the temperature.

In a similar manner, the heat capacity at constant pressure is defined by the equations:

$$c_{p\ \text{avg.}} = \frac{q_p}{T_2 - T_1} = \frac{H_2 - H_1}{T_2 - T_1} \tag{14}$$

and

$$c_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{15}$$

The heat capacity at constant volume c_v includes only the heat absorbed in increasing the internal energy, but the heat capacity at constant pressure c_p is larger because it includes in addition the work done in expansion against the surroundings.

Any two of the three variables, temperature, pressure, and volume, suffice to define the condition of a substance if E is a function only of T, p, and v. The change in the internal energy of a mole of gas may, therefore, be expressed by the fundamental equation of partial differentiation,

$$dE = \left(\frac{\partial E}{\partial T}\right)_v dT + \left(\frac{\partial E}{\partial v}\right)_T dv \tag{16}$$

where temperature and volume are the variables chosen. The derivative $(\partial E/\partial T)_v$ represents the heat absorbed per degree by the gas at constant volume and, therefore, according to equation 13, it may be replaced by c_v. Equation 16 now assumes the form:

$$dE = c_v\, dT + \left(\frac{\partial E}{\partial v}\right)_T dv \tag{17}$$

But since $dE = dq - dw$,

$$dq = c_v\, dT + \left(\frac{\partial E}{\partial v}\right)_T dv + dw$$

The work done when the volume of a mole of gas, liquid, or solid increases by an amount dv at pressure p is $p\, dv$. Hence,

$$dq_p = c_v\, dT + \left(\frac{\partial E}{\partial v}\right)_T dv + p\, dv$$

This equation means in words that the heat absorbed when a substance is heated slightly at constant pressure is equal to the sum of three quantities: (1) the temperature increase multiplied by the heat capacity at constant volume; (2) the volume increase multiplied by the rate at which the internal energy increases with volume, all other factors being held constant; (3) the work done in expansion.

Internal Energy of Gases. When an ideal gas expands into a vacuum in a closed system, there is no absorption or evolution of heat from the system as a whole. Since no external work is involved and since in an ideal gas there is no attraction between the molecules, there is no change in energy when the molecules become further separated. The situation may be understood by reference to **Fig. 35.**

Vessel A, provided with a thermometer, is filled with an ideal gas at pressure p_A, and vessel B of equal size is evacuated. When the stop-

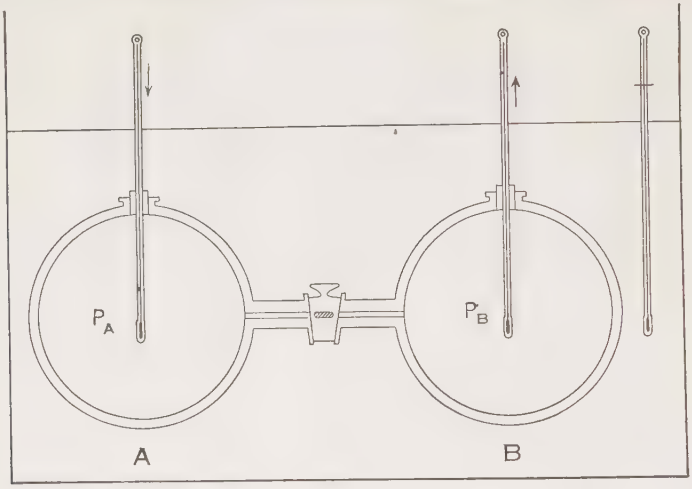


Fig. 35. Experiment on the internal energy of a gas.

cock is opened, gas rushes from A into B, and the temperature in A falls because the molecules are doing work in expanding into B against the pressure of the molecules which have previously entered from A. The temperature in B rises, as indicated on the thermometer, because the entering gas is being compressed. When equilibrium is reached and the pressure is the same in both vessels, the decrease in temperature in A is found to be exactly equal to the increase in temperature in B, and the temperature of the surrounding bath remains unchanged, as indicated by the third thermometer. The volume of the system $A + B$ is the same at the beginning and the end of the experiment, and so no *external* work is done against the surroundings.

Since $q = 0$ and $w = 0$, it follows, from equation 2, that ΔE must be zero. In other words, the internal energy of an ideal gas is independent of the volume, and

$$\left(\frac{\partial E}{\partial v}\right)_T = 0 \tag{18}$$

This equation gives an important criterion for an ideal gas.

The experiment shown in Fig. 35 was actually carried out in 1807 by Gay-Lussac and in a modified form in 1844 by Joule. They used air and other gases, but their experiments were not sufficiently sensitive to detect the thermal changes which actually do occur in real or nonideal gases.

Joule and Thomson were the first to devise an experiment which was able to detect the changes in internal energy which do occur when real gases are expanded. They applied pressure to a gas and forced it through a thermally insulated tube containing a porous plug of packed cotton and found that the temperature of most gases decreased after expansion through the porous plug but that the temperature of hydrogen increased. Their experiment can be understood by reference to **Fig. 36,** in which

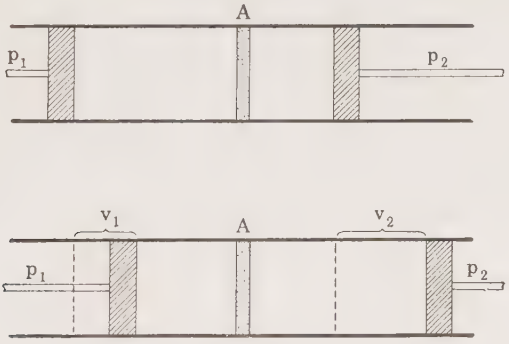


FIG. 36. The Joule-Thomson porous plug experiment.

two pistons operate in an insulated tube with a nonconducting porous plug between them. The piston at the left forces gas through the plug A at pressure p_1, and the volume decreases by an amount v_1, while at the same time the gas at the right, at a lower pressure p_2 increases in volume by an amount v_2. Both pressures remain constant, and the difference between the two represents the pressure necessary to overcome the resistance of the gas to flow through the porous plug. Then, the net work done by the system as a whole is the work of expansion p_2v_2, minus the work done in compression, or

$$w = p_2v_2 - p_1v_1$$

Since the system is thermally insulated, $q = 0$ and $\Delta E = -w$. Then

$$E_2 - E_1 = \Delta E = p_1v_1 - p_2v_2$$

or

$$E_2 + p_2v_2 = E_1 + p_1v_1$$

and, by equation 8,

$$H_2 = H_1$$

It is apparent then that in the expansion carried out in this way through a porous plug the enthalpy or heat content remains constant.

In this experiment, instead of the two pistons with small displacements, it is customary to pump through large quantities of gas and allow it to escape at atmospheric pressure. In this way a pronounced change of temperature, known as the Joule–Thomson effect, occurs when the gas passes through the plug. The Joule–Thomson coefficient μ is the change in temperature produced by the change in pressure of one atmosphere under conditions of constant enthalpy as defined by the expression,

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \tag{19}$$

The decrease in temperature on expansion through a porous plug is not due to the performance of external work but to the expansion against the attraction which exists between the molecules. For an ideal gas there is no attraction between molecules, and $\mu = 0$.

For air at atmospheric pressure and 0°, μ has the value +0.4, indicating that a decrease in pressure of 1 atm decreases the temperature 0.4°. For hydrogen and helium at room temperature, μ has negative values, or, in other words, these gases become warmer when forced through a porous plug. At temperatures below 154° K, however, μ becomes positive for hydrogen. It is evident that two factors are involved in the Joule–Thomson effect—an expansion against the force of attraction between the molecules (corresponding to a in van der Waals' equation), and a work term involving the change of pv with pressure. A more exact treatment is given in the appendix on page 676.

The Joule–Thomson coefficient μ has been determined accurately over a wide range of temperatures and pressures by Roebuck * and his coworkers for several gases. It is used not only in calculations for industrial processes such as the liquefaction of air but also for many thermodynamic quantities and the constants in equations of state for gases. One of the most accurate determinations of the relation of the centigrade scale to the absolute temperature scale depends on the experimental evaluation of μ.

Adiabatic Expansion of a Gas. An *adiabatic* process is one in which there is no loss or gain of heat, that is, one in which the system under investigation is thermally insulated from its environment. When a mole of gas expands adiabatically to a larger volume and a lower pressure, the volume is smaller than it would be under isothermal reversible ex-

* Roebuck, Murrell, and Miller. *J. Am. Chem. Soc.*, **64**, 400 (1942); also earlier contributions by Roebuck.

pansion to the same pressure, because in the adiabatic expansion the external work done cools the gas and leads to a shrinkage in volume, as shown in **Fig. 37.**

One mole of helium at A occupying 22.4 liters under 1 atm, and 0° expands isothermally to B where the volume is 44.8 liters at 0.5 atm still at 0°. When the mole of helium at A expands adiabatically toward C, at

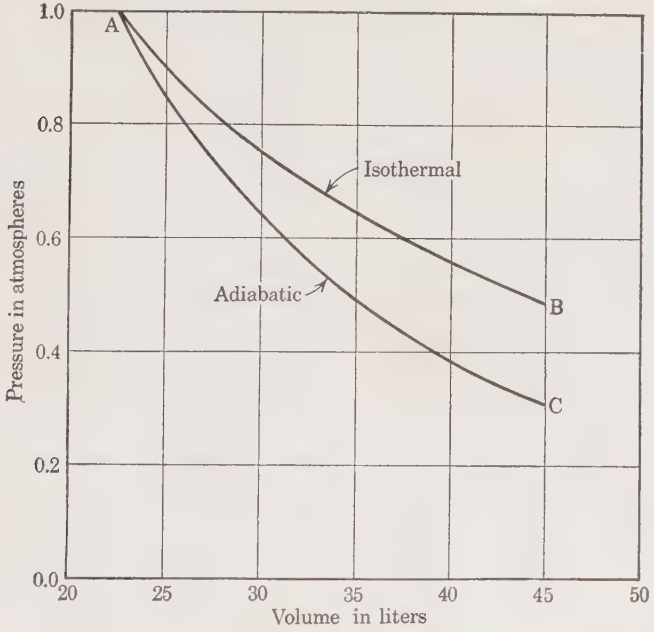


FIG. 37. Isothermal and adiabatic expansion of a gas.

0.5 atm it occupies 33.6 liters and the temperature falls to −66°. If it is allowed to expand still further to 44.8 liters at C, the temperature drops to −101°, and the pressure becomes 0.32 atm. The work done by the isothermal reversible expansion of the gas, represented by the area under AB, is larger than the work done by the adiabatic expansion, represented by the area under AC, indicating that the heat absorbed from the surroundings in the isothermal expansion supplies energy for doing work. The energy for the adiabatic expansion comes only from the internal cooling of the gas itself.

In the adiabatic expansion of a gas the temperature falls, but there is no exchange of heat with the surroundings, and $dq = 0$. Then, by the first law,

$$dE = dq - dw = -dw = -p\,dv$$

with reference to equations 17 and 18, $dE = C_v\,dT$ for the adiabatic expansion of 1 mole of an ideal gas, and, therefore,

$$C_v\,dT = -p\,dV$$

Since for 1 mole of an ideal gas, $p = RT/V$, it follows that

$$C_v\,dT = -RT\frac{dV}{V}$$

and

$$C_v\frac{dT}{T} = -R\frac{dV}{V}$$

If V_1 is the volume of the gas at the initial temperature T_1, and V_2 is the volume at the final temperature T_2, and if C_v is constant, integration between limits gives

$$C_v \ln\frac{T_2}{T_1} = -R \ln\frac{V_2}{V_1} \tag{20}$$

According to this equation, when 1 mole of an ideal gas having a heat capacity C_v expands reversibly and adiabatically, V_2 is greater than V_1, and, accordingly, T_2 must be less than T_1. In other words, the gas cools. It is evident also that adiabatic compression of the gas produces an increase in temperature. In solving problems it is necessary, of course, to express C_v and R in the same units.

Example 4. If a gas is compressed so rapidly that there is no opportunity to transfer heat to the container, the operation will be adiabatic. Calculate the temperature increase of a mole of helium which is compressed adiabatically from 44.8 liters at 0° to 22.4 liters. The molar heat capacity C_v of helium is constant and equal to 3.00 cal per degree.

$$C_v \ln\frac{T_2}{T_1} = -R \ln\frac{V_2}{V_1}$$

$$3.00 \times 2.303 \log\frac{T_2}{273.1} = -1.987 \times 2.303 \times \log\frac{22.4}{44.8}$$

$$\log T_2 = -\frac{1.987}{3.00}\left(\log\frac{1}{2}\right) + \log 273.1$$

$$T_2 = 432.4$$

$$\Delta T = 432.4 - 273.1 = 159.3°$$

Heat Capacity of Gases. When a monatomic gas, such as helium or mercury vapor, is heated at constant volume, the heat energy supplied is used only to augment the translational kinetic energy of the molecules. Since there is no change in volume, there can be no work done against

the atmosphere, and, since there is only one atom in the molecule, there can be no absorption of vibrational or rotational energy within the molecule.

According to the fundamental kinetic equation given on page 27,

$$pv = \tfrac{2}{3} \text{ kinetic energy} \tag{21}$$

or

$$\text{Kinetic energy} = \tfrac{3}{2}pv$$

But, for 1 mole of an ideal gas,

$$pV = RT = 1.987T$$

therefore,

$$\text{Kinetic energy of 1 mole} = \tfrac{3}{2}RT = 3T \quad \text{(approximately)} \tag{22}$$

If $3T_2$ represents the kinetic energy at temperature T_2, and $3T_1$ at temperature T_1, the difference in kinetic energy is $3(T_2 - T_1)$ cal. If now the difference in temperature is made exactly 1°, the difference in kinetic energy is 3 cal, and this value is the molar heat capacity at constant volume C_v, defined as the number of calories necessary to raise 1 mole of the gas through 1°. For gases in which the energy can be absorbed only by increasing the translational velocity,

$$C_v = 3 \text{ cal per degree per mole} \tag{23}$$

It has been found that monatomic gases have a molar heat capacity C_v of 3 cal per degree in perfect agreement with this formula.

When a gas is heated at constant pressure, the gas expands and does work against the atmosphere. Heat must be introduced into the gas to do this work as well as to raise the temperature. This work is equal to $p\,\Delta V$. If V_2 is the volume at T_2, and V_1 is the volume at T_1, and $T_2 - T_1 = 1°$, then for an ideal gas, in which the internal energy is independent of the volume,

$$C_p - C_v = p\,\Delta V = p(V_2 - V_1) = R(T_2 - T_1) = R$$
$$= 2 \text{ cal mole}^{-1} \text{ degree}^{-1} \tag{24}$$

Since $C_v = 3$ for monatomic gases, and $C_p = C_v + 2$, it follows that $C_p = 5$, and the ratio γ of the two heat capacities is

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.66 \tag{25}$$

Again, this relation is in excellent agreement with the experimental data for monatomic gases.

For polyatomic molecules the heat energy supplied is used not only in increasing the kinetic energy of translation in the three directions but also in increasing the energy of rotation and of vibration of the atoms within the molecule. If the extra energy absorbed is represented by g, then the ratio of the two specific heats will be

$$\gamma = \frac{C_p}{C_v} = \frac{5 + g}{3 + g} < 1.66 \tag{26}$$

The ratio becomes less than 1.66 in this case, and, with increasing complexity of the molecule, the value of g increases and the ratio γ becomes continuously smaller, but it cannot become less than 1.

In Table II the heat capacities of a few gases are given, and it will be

TABLE II

Molar Heat Capacities of Gases

(In cal per mole at 25° and at 1 atm)

Gas	C_p	C_v	$C_p/C_v = \gamma$
Argon, A	4.97	2.98	1.67
Helium, He	4.97	2.98	1.67
Mercury, Hg	4.97	2.98	1.67
Hydrogen, H_2	6.90	4.91	1.41
Oxygen, O_2	7.05	5.05	1.40
Nitrogen, N_2	6.94	4.95	1.40
Chlorine, Cl_2	8.25	6.14	1.34
Nitric oxide, NO	7.11	5.11	1.39
Carbon monoxide, CO	6.97	4.97	1.40
Hydrogen chloride, HCl	7.05	5.01	1.41
Carbon dioxide, CO_2	8.96	6.92	1.29
Nitrous oxide, N_2O	9.33	7.29	1.28
Sulfur dioxide, SO_2	9.4	7.3	1.29
Ammonia, NH_3	8.63	6.57	1.31
Methane, CH_4	8.60	6.59	1.31
Ethane, C_2H_6	12.71	10.65	1.19
Dimethyl ether, C_2H_6O	15.89	13.75	1.16

seen that, for monatomic gases, $C_v = 3$ and $\gamma = 1.66$; that, for all gases, C_p is greater than C_v by about 2 cal per degree; that C_p increases and γ decreases as the molecules increase in molecular weight and involve more atoms with additional opportunities for different types of vibration within the molecule.

There is nothing in equation 23 to indicate that the heat capacity of a monatomic gas is affected by temperature, but, in equation 26 for polyatomic gases, it can be seen that, if g changes with temperature, both the heat capacities and their ratios may be influenced by a temperature change. In agreement with these theoretical deductions, the molar heat capacity C_p of monatomic gases is found to be 5 cal degree^{-1} mole^{-1} at all temperatures, but the heat capacity of polyatomic gases increases with increasing temperature, as shown in **Fig. 38.** In general, the more

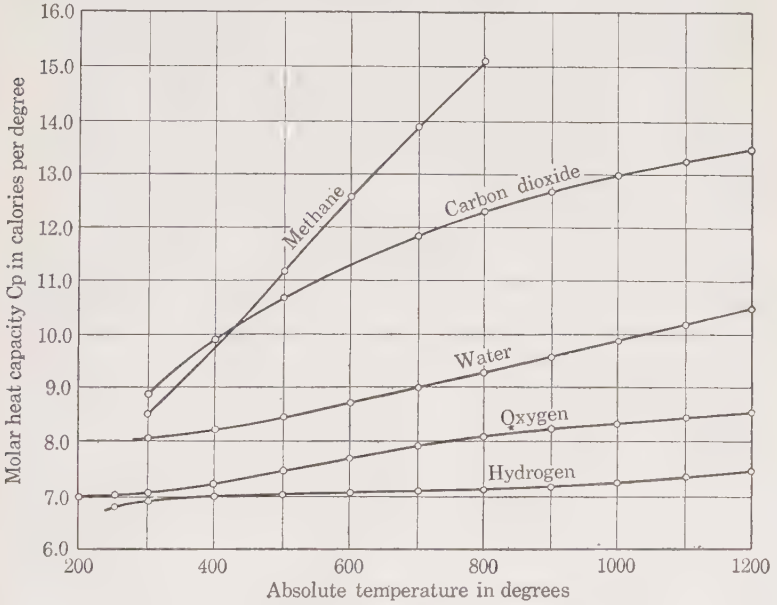


FIG. 38. Influence of temperature on heat capacity of gases.

complex the molecule is, the greater is its molar heat capacity, the greater is the temperature effect, and the steeper is the slope of the line when plotted as in Fig. 38. The molar heat capacity C_p of helium would be indicated by a horizontal line at 5.0.

The deductions concerning the relation between increasing molar heat capacity and molecular complexity are supported not only by the few examples given in Table II but also by an examination of many gases. One of the most striking experimental supports of these deductions is found in the heat capacity of hydrogen. At temperatures below 60° K the diatomic gas H_2 behaves as a monatomic gas and γ is found to have a value of 1.66, showing that the extra internal energy not only decreases with decreasing temperatures but actually disappears.

A table of constants for calculating the heat capacities of the common gases at different temperatures is given on page 135.

Attempts have been made to express the "complexity of the molecule" in more quantitative terms. A diatomic molecule with the atoms joined in a fixed position can absorb rotational energy by turning over on its axis, and it can absorb vibrational energy by oscillation of the atoms within the molecule. In complex molecules there can be rotations and different types of oscillation between different pairs or groups of atoms. These different ways of absorbing energy correspond to *degrees of freedom.*

Theoretically it is possible to calculate a maximum value for the contribution of a degree of freedom to the molar heat capacity. Thus, it was shown in equation 22 that the translational energy in the three directions of space for a mole of gas is $\frac{3}{2}RT$, and, therefore, the energy in one direction is $\frac{1}{2}RT$. This one direction is actually one degree of freedom. As a first approximation, it may be estimated that each translational and each rotational degree of freedom contributes $\frac{1}{2}RT$ to the internal energy or $\frac{1}{2}R$ to the heat capacity, but the vibrational degrees of freedom each contribute somewhere between O and RT to the internal energy or between O and R to the heat capacity.

As already mentioned, all polyatomic gases decrease in heat capacity at lower temperatures, that of hydrogen actually falling to the value of a monatomic gas, but there is no satisfactory explanation on the basis of ordinary mechanics. This tendency for some of the degrees of freedom to "freeze up" at low temperatures and the quantitative way in which it affects the heat capacity depend on rules which have been partly worked out with the help of the quantum theory and which are discussed briefly on page 569.

Heat Capacity of Solids. Studies of the specific heats of solids at extremely low temperatures have resulted in the formation of several interesting relationships between heat capacity and temperature. Einstein, Debye, and Nernst and Lindemann have pioneered in this field.*

The degrees of freedom of internal vibration tend to freeze up at low temperatures not only for gases but for liquids and solids as well. The amplitude of the internal vibrations of atoms and groups within a crystal becomes very small as the absolute zero is approached. Under these conditions, the crystal may vibrate as a single unit and behave as a single large molecule.

The equation of Debye for the molar heat capacity of crystals in the neighborhood of the absolute zero is based on this assumption that the

* Einstein, *Ann. Physik*, [4] **22,** 180 (1907); Debye, ibid., [4] **39,** 789 (1912).

crystal is a perfectly elastic body vibrating as a single unit. It is

$$C_v = 465 \frac{T^3}{\theta^3} \text{ cal per mole}$$

where 465 cal per mole is a constant and θ is a constant, having the dimensions of temperature, which is characteristic for a particular crystal or class of crystals. For example, the value of θ for carbon is 1860, and for copper it is 315. The larger the value of θ, the greater is the temperature range above absolute zero in which the Debye formula gives satisfactory results. Usually the equation is not useful above 50° to 75° K, but it is in this region that experimental measurements are difficult and this equation is useful. The heat capacity of most crystals approaches zero at absolute zero in agreement with the formula.

Debye's equation does not apply at higher temperatures since the solid is no longer vibrating as a single unit. The lighter the atoms and the greater the crystalline forces within the solid, the higher is the temperature required for the individual atoms to acquire appreciable independent kinetic energy.

At room temperatures most of the solid elements, except those of low atomic weight, have reached a temperature at which all the different ways of absorbing heat are utilized, and they have the limiting value of atomic heat capacity, as shown in **Fig. 39.** In 1819 Dulong and Petit

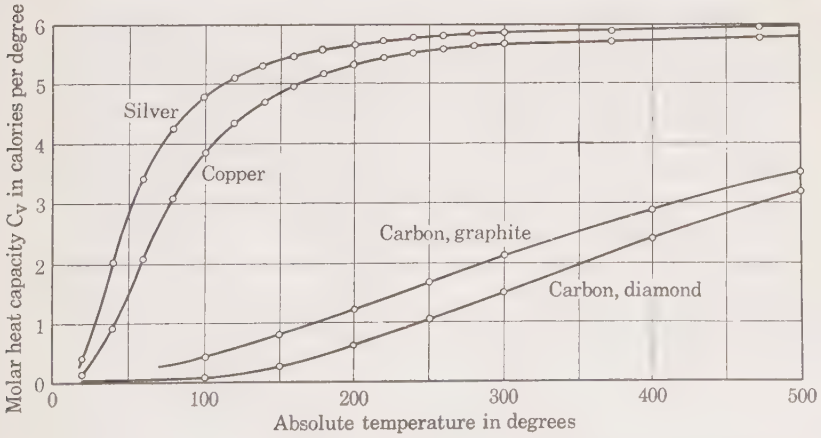


FIG. 39. Molar heat capacity of solid elements as a function of temperature.

discovered the important fact that *the product of the specific heat c_p and the atomic weight of the solid elements is a constant, approximately 6.4.* This law of Dulong and Petit played an important part in the determination of atomic weights, for it served to show from a simple specific-heat

measurement what multiple of the combining weight should be taken for the atomic weight in order to obtain the constant 6.4.

Lewis has shown that the specific heat at constant volume is a more significant quantity than the specific heat at constant pressure. In the latter case, there are secondary effects depending on the thermal expansion and compressibility which tend to mask the more fundamental relation. Lewis and Gibson * found that the atomic heat capacity at constant volume and room temperature is 5.9 within 0.09 for all the elements heavier than potassium for which data were available.

It may be noted that this value of 5.9 for the atomic heat capacity of a crystal is nearly three times the gas constant. Moreover, it may be remembered that the heat capacity of a monatomic gas at constant volume is $\frac{3}{2}R$. There is a theoretical reason why the atomic heat capacity of a crystal should be twice that of a monatomic gas. In a monatomic gas, heat is absorbed only in giving the molecule increased kinetic energy, but, in a crystal, the units of the lattice have definite positions, and, when they are displaced, they acquire potential energy which is equal to the kinetic energy required to displace them. Twice as much heat energy then is necessary to raise the temperature 1°.

The influence of temperature on the heat capacity of crystals is shown in Fig. 39 for three different elements. Near the absolute zero of temperature, all the crystals increase in heat capacity slowly, in agreement with the Debye theory, and, then, at higher temperatures, the heat capacity increases rapidly with the temperature as new vibrations are brought into action and new degrees of freedom are released. Finally, at sufficiently high temperatures, the limiting Dulong and Petit value of 5.9 is reached. It occurs at low temperatures for those elements like lead which are soft and malleable and have large atomic weights and low melting points. These properties indicate that the atoms are held together rather loosely in the crystal and can vibrate internally in all possible directions with an expenditure of energy which is available at temperatures well below room temperature. Carbon, however, has strong crystal forces as evidenced by the fact that it has a very high melting point. Moreover, it has a low atomic weight. These properties lead to atomic vibrations of such high energy that it is necessary to heat carbon to a very high temperature before there is enough energy to bring all the vibrations into play. Accordingly, the full atomic heat capacity of 5.9 cal at constant volume is not reached even at moderately high temperatures.

These differences in behavior are now interpreted in terms of the

* Lewis and Gibson, *J. Am. Chem. Soc.*, **39**, 2554 (1917).

quantum theory (Chapter XIX) and for simple molecules can be calculated quantitatively from spectrographic data.

At very high temperatures the thermal agitation of the atoms may become so great as to impart some energy to the electrons, and, accordingly, under these conditions some metals like iron, which hold their electrons rather loosely and which remain solid at high temperatures, possess atomic heat capacities greater than 5.9 cal per degree.

The molar heat capacities of crystalline compounds can be estimated approximately by adding up the molar heat capacities of the elements. For example, the molar heat capacity of lead sulfide PbS is 12.3 at room temperature, and the sum of the gram-atomic heat capacities of lead and sulfur is 6.3 + 5.5 or 11.8.

REFERENCES

Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

Glasstone, "Thermodynamics for Chemists," D. Van Nostrand Co., New York, 1947.

Steiner, "Introduction to Chemical Thermodynamics," McGraw-Hill Book Co., New York, 1941.

Butler, "Fundamentals of Chemical Thermodynamics," Macmillan Co., New York, Part I, 1928; Part II, Second Edition, 1935.

PROBLEMS

1. A 900-g weight falls 120 m. (*a*) How many ergs of heat are liberated when it strikes the ground? (*b*) How many joules? (*c*) How many calories? (*d*) How many liter-atmospheres?

Ans. (*a*) 1.059×10^{10} ergs. (*b*) 1059 joules. (*c*) 253.1 cal. (*d*) 10.45 liter-atm.

2. Calculate the work done when a mole of sulfur dioxide gas expands isothermally and reversibly at 27° from 10 atm to 1 atm:

(*a*) Assuming that the gas is an ideal gas.

(*b*) Would an attractive force between molecules of the gas tend to make the work done larger or smaller? *Ans.* (*a*) 1370 cal.

3. How many calories of heat is required to raise the temperature of 10 g of argon (a monatomic gas) through 10° (*a*) at constant volume? (*b*) at constant pressure?

Ans. (*a*) 7.5 cal. (*b*) 12.5 cal.

4. Lead chloride is found by chemical analysis to contain 74.5 per cent lead and 25.5 per cent chlorine. The atomic weight of chlorine is 35.45. The specific heat of lead is approximately 0.030. Using this information, decide between the possible formulas such as Pb_2Cl, PbCl, $PbCl_2$, $PbCl_3$, etc., and calculate the atomic weight of lead. *Ans.* $PbCl_2$; 207.2.

5. (*a*) When a gas is heated at constant volume all the heat is used in increasing the internal energy E of the gas, and, when the gas is an ideal monatomic gas, the only change is an increase in the kinetic energy of the molecules, the formula for

which is known. Prove by differential calculus that for an ideal monatomic gas $C_v = 3$ cal mole^{-1} deg^{-1}.

(*b*) At constant pressure the heating of a gas produces work in addition to the increase in internal energy. Show by differential calculus that for an ideal monatomic gas $C_p = C_v + R$.

6. Prove for the case of a piston moving in a cylinder that the work done equals the pressure times the cross-sectional area times the distance, using the fundamental relation that work equals force times distance.

---

7. A 150-lb man walks up a flight of stairs 60 ft high. How much work does he do in (*a*) ergs and (*b*) calories?

8. One hundred grams of liquid benzene is vaporized at its boiling point 80.2° at 760 mm. The heat of vaporization at constant pressure is 94.4 cal per gram. Calculate (*a*) w; (*b*) q; (*c*) ΔH; (*d*) ΔE. (*e*) Is w the maximum work that can be performed?

9. Show that for an isothermal expansion of an ideal gas $\Delta H = 0$.

10. One hundred grams of benzene vapor (free from liquid benzene) at 80.2° and 760 mm is expanded isothermally by reducing the pressure to 100 mm. Assume that benzene vapor acts as an ideal gas.

(*a*) What is the maximum work that can be obtained by this expansion?

(*b*) What is the maximum work that can be obtained by expanding 100 g of benzene isothermally at 100° from 760 mm to 100 mm?

11. Ten liters of mercury vapor which is monatomic, expands adiabatically at 600° from 3 atm until the pressure is 1 atm. What will be the temperature of the mercury vapor after the adiabatic expansion?

12. Estimate the maximum rise in temperature of a 500-kg iron weight when it hits a hard iron surface after falling through 500 m (neglecting air resistance and assuming that half the heat goes into the iron weight). The atomic weight of iron is 55.85.

13. The specific heat of zinc is 0.0978, and it has been established that 10.00 g of zinc combine with 10.85 g of chlorine to form a stable zinc chloride.

What is the atomic weight of zinc, and what is the formula for the zinc chloride if the valence of chlorine is one and its atomic weight 35.45?

14. Calculate the molar heat capacity of glycol, $(CH_2OH)_2$, at 2° from the data. One hundred grams of glycol was weighed into a copper container equipped with an electric heater and a sensitive resistance thermometer. The copper container or calorimeter was suspended by fine cords inside a metal shield which was in turn suspended inside an outer container which could be evacuated. The shield carried heaters and thermocouples by means of which its temperature was kept so close to that of the calorimeter that the heat leak to the calorimeter was negligible. The apparatus was immersed in an ice bath, and, after it had cooled to nearly 0°, it was evacuated. With the shield maintained at the temperature of the calorimeter, 955 absolute joules was required to heat the calorimeter from 0.500° to 3.500°. In a similar experiment the heat capacity of the calorimeter was found to be 20.00 cal per degree at 2°.

15. A mole of ammonia gas is condensed at its boiling −33.4° C by the application of a pressure infinitesimally greater than 1 atm. To evaporate a gram of ammonia at its boiling point requires the absorption of 327 cal. Calculate (*a*) w; (*b*) q; (*c*) ΔH; (*d*) ΔE.

16. One hundred liters of water vapor at 100° and $\frac{1}{2}$ atm is compressed isothermally and reversibly to 1 atm and further until the volume is 10 liters. Neglecting the

volume of the water condensed in comparison with the volume of the vapor and assuming that the vapor behaves as an ideal gas, calculate the work done and the heat evolved.

17. Ten cubic feet of oxygen under pressure is allowed to expand reversibly under adiabatic conditions to a volume of 30 cu ft. Considering oxygen to be an ideal gas with the average heat capacity given in the table, calculate the final temperature if the initial temperature is 25°.

18. The specific heat of neon at constant volume is 0.149, and the ratio $c_p/c_v = 1.66$. How many atoms are there in a molecule of neon?

19. One mole of an ideal gas is confined in a cylinder by a piston. The pressure is p, the volume is V, and the cylinder is immersed in a thermostat at temperature T. The following cycle is carried out: (1) The temperature of the thermostat is raised 1°, the pressure being kept constant; (2) the pressure is gradually increased until the volume is decreased to the original value V, with no change in temperature; and (3) the temperature of the thermostat is lowered 1°, the volume being kept constant. Make a table showing the initial and final pressure, volume, and temperature, and q, w, and ΔE, for each step. Since ΔE for the cycle is 0, show that $C_p - C_v = R$.

20. Estimate how many more calories of heat will be required to heat 100 g of aluminum from 25 to 300° than will be required to heat the same weight of silver through the same temperature interval.

---

21. For the adiabatic expansion of a perfect gas show that

$$pV^{\gamma} = \text{constant}$$

and that

$$TV^{R/C_v} = \text{constant}$$

22. Develop a formula for calculating $C_p - C_v$ for a gas which follows van der Waals' equation.

23. A perfect monatomic gas passes from a large pipe into an evacuated cylinder through a valve which is opened slowly enough to keep the pressure in the pipe sensibly constant. The gas in the main is at pressure P and temperature T. Develop a formula for calculating the temperature of the gas in the cylinder when its pressure reaches the pressure P' of the pipe, if the gas loses no heat during the process.

24. What is the minimum number of calories of work required to compress isothermally 1 mole of ammonia at 1 atm and 150° to a volume of 10 liters: (*a*) assuming that it follows the ideal-gas laws, (*b*) assuming that it follows van der Waals' equation with the constants given in Table II on page 16?

CHAPTER VII

THERMOCHEMISTRY

Definitions. Thermochemistry is concerned with the heat which accompanies chemical reaction.

The different units of heat energy are related by definition as follows:

$$1 \text{ calorie (cal)} = 0.001 \text{ kilocalorie (kcal)} = 4.1840 \text{ absolute joules}$$

Thermochemical data are usually expressed by writing the equation for the reaction and giving the value of ΔH for the reaction. For example,

$$C + O_2 = CO_2 \qquad \Delta H = -94{,}030 \text{ cal}$$

It will be remembered that ΔH is the heat of reaction at constant pressure. In chemical equations it is the change in enthalpy when the reactants, that is, the chemical compounds written at the left of the equation, react to give the reaction products written at the right of the equation. The absolute values of the enthalpy are unknown and unnecessary. In the oxidation of carbon, heat is evolved, and the enthalpy is thereby decreased, so that ΔH has a negative value. As a matter of fact, most ordinary chemical reactions evolve heat. They are *exothermic* reactions and have negative values of ΔH. At temperatures much higher than ordinary room temperatures the heat-absorbing or *endothermic* reactions are more common.

In writing equations, solids, liquids, and gases are designated by (s), (l), and (g), respectively, and the preceding equation is written

$$C\ (s) + O_2\ (g) = CO_2\ (g) \qquad \Delta H = -94{,}030 \text{ cal}$$

If the units are not specified, it may be assumed that ΔH is expressed in calories.

Sometimes the symbols l, s, and g are omitted when there is no chance of confusion.

Another convention used in the thermochemistry of solutions is the symbol aq (*aqua*, water) signifying a large excess of water, so large that the addition of more water has no measurable effect on the temperature.

Calorimetric Measurements. Calorimeters are used for measuring the heat changes which accompany chemical reactions. In the most

common type, the reaction is allowed to take place in a reaction chamber surrounded by a weighed quantity of water in an insulated vessel, and the rise in temperature is measured with a sensitive thermometer. The product of the rise in temperature and the total heat capacity of the water and calorimeter is a measure of the heat evolved. The heat capacity of the surrounding water is obtained by weighing the water, and the heat capacity of the calorimeter is obtained by measuring a reaction of known heat evolution, or by introducing a measured quantity of heat with an electric heater. The best reactions to measure are those which proceed rapidly, thus minimizing any errors due to cooling; and those which run to completion, thus assuring that the heat value obtained applies to the reaction assumed and that none of the reacting materials remain unreacted.

The water in the calorimeter must be stirred adequately to insure uniform temperature throughout, but the heat of stirring must be kept to a minimum so that corrections from this source will be small. The evaporation of the water must be kept very small also. The heat lost from the hotter calorimeter to its surrounding jacket may be calculated by plotting the temperature of the calorimeter against time, and extrapolating this cooling curve back to the time at which the heat-evolving reaction started. The difference between this extrapolated temperature and the initial temperature gives a fair estimate of the temperature rise which would have been obtained if there had been no loss of heat from the calorimeter during the period of observation.

In adiabatic calorimetry the cooling correction is rendered unnecessary by experimental devices which eliminate or greatly reduce the transfer of heat. Vacuum-walled vessels are used to minimize the heat losses, or the outer jacket is heated electrically at an experimentally controlled rate such that the temperature of the jacket is kept always at the same temperature as the calorimeter.

Laws of Thermochemistry. The *heat evolved in a given reaction is equal to the heat absorbed in the reverse reaction.* The quantity of heat absorbed in decomposing a chemical compound must be equal to the heat evolved in its formation, provided that the materials involved in the two reactions are present in the same quantities and are under the same physical and chemical conditions. This law was first stated in 1780 by Lavoisier and Laplace. It is an expression of the more general law of the conservation of energy.

According to another law of thermochemistry, propounded first by Hess in 1840, *the heat of a chemical reaction at constant pressure is independent of the number of intermediate steps involved.* Since the total value of enthalpy ΔH for the reaction depends only on the initial and final

state, it is not affected by the path followed in passing from the initial to the final state.

This law of constant heat summation may be illustrated with the heat of formation of ammonium nitrate in aqueous solution, when prepared in two different ways. The total amount of heat evolved in the formation and solution of ammonium nitrate is the same within experimental error whether gaseous ammonia and liquid nitric acid are allowed to react and the resulting product is dissolved in water or whether the ammonia and nitric acid are dissolved in water and then allowed to react. Thus, the following reactions may be added to give the over-all reaction:

$$\begin{aligned} NH_3\ (g) + HNO_3\ (l) &\rightarrow NH_4NO_3\ (s) & \Delta H &= -34.66 \\ NH_4NO_3(s) + aq &\rightarrow NH_4NO_3(aq) & \Delta H &= \quad 6.31 \\ \hline NH_3\ (g) + HNO_3\ (l) + aq &\rightarrow NH_4NO_3\ (aq) & \Delta H &= -28.35 \end{aligned}$$

or, alternatively, the following two reactions may be added to give the same over-all reaction:

$$\begin{aligned} NH_3\ (g) + aq &\rightarrow NH_3\ (aq) & \Delta H &= -\ 8.48 \\ HNO_3\ (l) + aq &\rightarrow HNO_3\ (aq) & \Delta H &= -\ 7.45 \\ NH_3\ (aq) + HNO_3\ (aq) &\rightarrow NH_4NO_3\ (aq) & \Delta H &= -12.23 \\ \hline NH_3\ (g) + HNO_3\ (l) + aq &\rightarrow NH_4NO_3\ (aq) & \Delta H &= -28.16 \end{aligned}$$

It is to be noted that in adding up thermochemical equations the equations are so chosen that the intermediate compounds formed, such as NH_4NO_3 (s), NH_3 (aq), and HNO_3 (aq), occur in equal quantities on each side of the equality sign and thus cancel out. Only the desired reactants and products remain and the heat of the over-all reaction, the heat of reaction at constant pressure, is obtained by adding up the ΔH's for all the steps. The reactions for which the values of ΔH are known are written down directly or in the reverse direction in such a way that the extra compounds not involved in the desired reaction will cancel out. When the reaction is reversed, the value of ΔH will be reversed in sign. It may be necessary to try out several different equations, choosing from among the rapid reactions which have been accurately measured. When a suitable set of equations is found, all the values of ΔH are added together algebraically.

This law of constant heat summation is convenient for determining the heat of a reaction which cannot be measured by direct experimental methods. Thus, it is not practical to measure the heat evolved when

carbon burns to carbon monoxide in a limited amount of oxygen because the product will be an uncertain mixture of carbon monoxide and carbon dioxide. However, it is a simple matter to burn the carbon completely to carbon dioxide in an excess of oxygen and to measure the heat of this complete reaction. Thus,

$$C\ (s) + O_2\ (g) = CO_2\ (g) \qquad \Delta H = -94.03 \text{ kcal}$$

The heat evolved when carbon monoxide burns to carbon dioxide can be readily measured also:

$$CO\ (g) + \tfrac{1}{2}O_2\ (g) = CO_2\ (g) \qquad \Delta H = -67.64 \text{ kcal}$$

Writing these equations in such a way as to obtain the desired reaction $C + \frac{1}{2}O_2 = CO$, adding and canceling

$$\begin{array}{lr} C\ (s) + O_2\ (g) = CO_2\ (g) & \Delta H = -94.03 \text{ kcal} \\ CO_2\ (g) = CO\ (g) + \tfrac{1}{2}O_2\ (g) & \Delta H = 67.64 \text{ kcal} \\ \hline C\ (s) + \tfrac{1}{2}O_2\ (g) = CO\ (g) & \Delta H = -26.39 \text{ kcal} \end{array}$$

The indirect calculation of heats of reaction is illustrated with another example.

Example 1. What is the heat of reaction when sulfuric acid is formed from its elements?

It is not possible to mix hydrogen and oxygen and sulfur in a calorimeter and produce sulfuric acid directly, but reactions which are capable of direct calorimetric measurements can be selected in such a way that, when added together, they will give the desired over-all reaction.

Sulfur is burnt in a stream of oxygen in a calorimeter at room temperature.

Sulfur dioxide is oxidized with oxygen with a platinum catalyst at a high temperature, and the corrections are made to give the heat of reaction at room temperature. Other necessary reactions are included. Then

$$\begin{array}{lr} S\ (s) + O_2\ (g) = SO_2\ (g) & \Delta H = -69.3 \text{ kcal} \\ SO_2\ (g) + \tfrac{1}{2}O_2\ (g) = SO_3\ (s) & \Delta H = -22.3 \text{ kcal} \\ SO_3\ (s) + H_2O\ (l) = H_2SO_4\ (l) & \Delta H = -30.0 \text{ kcal} \\ H_2\ (g) + \tfrac{1}{2}O_2\ (g) = H_2O\ (l) & \Delta H = -68.4 \text{ kcal} \\ \hline S\ (s) + 2O_2\ (g) + H_2\ (g) = H_2SO_4\ (l) & \Delta H = -190.0 \text{ kcal} \end{array}$$

Heats of Formation. Although the absolute enthalpy or heat content of compounds may be unknown, the *heats of formation* can be cal-

culated by arbitrarily assuming that the enthalpy of the elements in their standard states is zero. For example, it follows from the reaction,

$$C\ (s) + O_2\ (g) = CO_2\ (g) \qquad \Delta H = -94.03 \text{ kcal}$$

that the heat of formation of carbon dioxide is $-94{,}030$ cal, because 94,030 cal of heat is evolved when a mole of carbon dioxide gas is produced from the elements, and the elements are arbitrarily assigned a zero value. The symbol ΔH_f is used for the heat of formation of a compound at constant pressure; it is the difference in enthalpies or heat contents of the compound and the elements from which it is formed. The enthalpy of the elements will vary, depending on their physical state, and it is conventionally agreed that the standard states for which H is taken as zero are the naturally occurring states of the elements under 1 atm pressure and at the temperature of the reaction. In the example given, oxygen is a gas at atmospheric pressure, and carbon is a solid. Unless the temperature is specified, it is assumed to be 25° C. If two or more allotropic forms can exist at the specified temperature, it is necessary to specify the form. In this book graphite is always taken as the standard state for carbon and rhombic sulfur as the standard state for sulfur.

The heats of formation of several inorganic and organic compounds are collected for reference in Table I.

The calculation of heats of reaction is simplified by using the heats of formation when they are available. The change in enthalpy of a given reaction ΔH is obtained by subtracting the heats of formation ΔH_f of the reactants from those of the products.

$$\begin{array}{cccccc} Fe_2O_3\ (s) & + & 2Al\ (s) & = & Al_2O_3\ (s) & + & 2Fe\ (s) \\ -198.5 & & 0 & & -399.0 & & 0 \end{array}$$

where the heats of formation of the compounds are given below each compound. Then,

$$\Delta H = (-399.0 + 0) - (-198.5 + 0) = -200.5 \text{ kcal}$$

In the same way the heats of formation may be calculated from measured heats of reaction, thus:

$$C_6H_6\ (l) + 7\tfrac{1}{2}O_2\ (g) = 6CO_2\ (g) + 3H_2O\ (l) \qquad \Delta H = -781.4 \text{ kcal}$$

$$\Delta H = -781.4 = (\Delta H_f)_2 - (\Delta H_f)_1$$

$$= [6 \times (-94.0) + 3 \times (-68.3)] - (\Delta H_f)_1$$

$$(\Delta H_f)_1 = 781.5 - 768.9 = 12.5 \text{ kcal}$$

TABLE I

Heats of Formation at 25°

ΔH_f in kcal per mole

Inorganic Compounds

Na_2O	−99.5	$MgCl_2$	−153.3	$PbSO_4$	−218.5
Al_2O_3	−399.0	$PbCl_2$	−85.7	HCl (*g*)	−22.1
CaO	−151.8	NaBr	−86.7	HBr (*g*)	−8.7
FeO	−64.3	KBr	−94.1	HI (*g*)	+5.9
Fe_2O_3	−198.5	AgBr	−23.8	H_2O (*l*)	−68.3
Fe_3O_4	−266.9	$PbBr_2$	−66.3	H_2O (*g*)	−57.8
PbO	−52.5	NaI	−69.3	D_2O (*l*)	−70.4
Ag_2O	−7.0	KI	−78.9	D_2O (*g*)	−59.6
HgO	−21.6	AgI	−14.9	NH_3 (*g*)	−11.0
Na_2S	−89.8	PbI_2	−41.8	SO_2 (*g*)	−70.9
K_2S	−121.5	$NaNO_3$	−111.7	H_2SO_4 (*l*)	−193.8
PbS	−22.3	KNO_3	−118.1	N_2O (*g*)	+19.7
NaCl	−98.3	$AgNO_3$	−29.4	NO (*g*)	+21.6
KCl	−104.4	$Pb(NO_3)_2$	−106.9	HNO_3 (*l*)	−41.7
$BaCl_2$	−205.3	Na_2SO_4	−330.5	C (diamond)	+0.5
$FeCl_2$	−81.9	K_2SO_4	−342.7	CO (*g*)	−26.4
$FeCl_3$	−96.4	$BaSO_4$	−349.4	CO_2 (*g*)	−94.0

Organic Compounds

Methane, CH_4 (*g*)	−17.9	Cyclohexene, C_6H_{10} (*l*)	−14.8
Ethane, C_2H_6 (*g*)	−20.2	Benzene, C_6H_6 (*l*)	+12.3
Propane, C_3H_8 (*g*)	−24.8	Thiophene, C_4H_4S (*l*)	+19.6
n-Butane, C_4H_{10} (*g*)	−29.7	Methanol, CH_3OH (*l*)	−57.0
iso-Butane, C_4H_{10} (*g*)	−31.4	Ethanol, C_2H_5OH (*l*)	−66.3
n-Pentane, C_5H_{12} (*g*)	−34.8	*n*-Propanol, C_3H_7OH (*l*)	−73.1
n-Pentane, C_5H_{12} (*l*)	−41.1	*n*-Butanol, C_4H_9OH (*l*)	−79.5
n-Hexane, C_6H_{14} (*l*)	−47.6	Glycerol, $C_3H_8O_3$ (*l*)	−158.6
n-Heptane, C_7H_{16} (*l*)	−53.9	Formic acid, CH_2O_2 (*l*)	−99.5
n-Octane, C_8H_{18} (*l*)	−60.3	Acetic acid, $C_2H_4O_2$ (*l*)	−116.7
Cyclohexane, C_6H_{12} (*l*)	−37.7	Oxalic acid, $C_2H_2O_4$ (*s*)	−196.7
Ethylene, C_2H_4 (*g*)	+12.6	Succinic acid, $C_4H_6O_4$ (*s*)	−224.8
Propylene, C_3H_6 (*g*)	+4.8	Fumaric acid, $C_4H_4O_4$ (*s*)	−194.1
n-Butene-1, C_4H_8 (*g*)	+0.3	Maleic acid, $C_4H_4O_4$ (*s*)	−188.6
n-Pentene-1, C_5H_{10} (*g*)	−5.0	Benzoic acid, $C_7H_6O_2$ (*s*)	−91.7

Inasmuch as ΔH for the reactants is 12.5 kcal and ΔH_f for oxygen or for any element is zero, the heat of formation ΔH_f of liquid benzene from carbon (graphite) and hydrogen gas at 1 atm is 12.5. In other words, if hydrogen and graphite could combine under these conditions, there would be an absorption of 12.5 kcal of heat.

Reactions at Constant Pressure and Constant Volume. As explained on page 104, when a reaction occurs at constant volume, no work is involved, but, if the system is allowed to expand during the reaction, it does work against the atmosphere, and a smaller quantity of heat is evolved. If the system contracts, the heat evolved in a reaction at constant pressure is greater than that at constant volume by an amount equal to the work done on the system by the surroundings. If the products and the reactants have the same volume, the heats of reaction at constant pressure are the same as those at constant volume.

The general equation relating ΔH and ΔE is given here:

$$\Delta H = \Delta E + p\,\Delta v = \Delta E + \Delta n\,RT \qquad (1)$$

where ΔH is the heat of reaction at constant pressure, ΔE is the heat of reaction at constant volume, and $p\,\Delta v$ is the work done by the system. Since liquids and solids occupy very small volumes, the term $p\,\Delta v$ usually includes only the volumes of gases. The increase in the number of moles of gas is denoted by Δn, that is, the number of moles of gaseous products minus the number of moles of gaseous reactants. This equation is exact only when the gases are ideal, but for practical purposes it is satisfactory for all gases at atmospheric pressure.

Heats of reaction are usually given for conditions of constant pressure because most reactions are studied at constant pressure. Heats of combustion of liquids and solids, however, are usually measured at constant volume, and equation 1 is useful in converting one into the other.

Example 2. The heat of combustion of benzene at constant volume is 780.5 kcal.

$$C_6H_6\,(l) + 7\tfrac{1}{2}O_2\,(g) \rightarrow 6CO_2\,(g) + 3H_2O\,(l) \qquad \Delta E = -780.5 \text{ kcal}$$

What is the value of ΔH, that is, the heat of reaction at constant pressure?

$$\begin{aligned}\Delta H = \Delta E + \Delta n\,RT &= -780{,}500 - 1.5 \times 1.987 \times 298.1 \\ &= -780{,}500 - 889 = -781{,}389 \\ &= -7.814 \times 10^5 \text{ cal} = -781.4 \text{ kcal}\end{aligned}$$

The number $-781{,}389$ should not be written as a final value, because it implies that the result is known with an accuracy of one part in 781,389, whereas the experimental errors are so great that the value should not be expressed beyond four significant figures.

Heat of Combustion. The heat evolved in the complete oxidation of a substance is known as the *heat of combustion*. The values are given in terms of heat of combustion per gram, or as heats of combustion per mole. Since only rapid complete reactions are suitable for thermochemical measurement, heats of combustion have been by far the most common data of thermochemistry. A great deal of our present thermochemical knowledge goes back to the data of Thomsen and Berthelot of the last century. Richards and his coworkers made many measurements of much greater accuracy. For details of recent measurements and calculations, the literature * should be consulted.

It is essential to burn everything to its highest stage of oxidation to insure that a definite reaction is being measured which will give reproducible results. For this purpose the material is ignited electrically in a heavy steel bomb containing oxygen under a pressure of 25 atm. All carbon is burnt to carbon dioxide and all hydrogen to water. As yet the halogen-containing compounds present difficulties, and the heat of combustion of a substance like ethyl chloride is not known with high accuracy because the products formed are not always definite.

Example 3. Calculate the heat change involved when 1 mole of monoclinic sulfur is converted into rhombic sulfur at room temperature. Although there is a natural transition at room temperature, the change is too slow for accurate calorimetric measurements. Accordingly, the two different forms are subjected to a reaction, the heat of which can be measured accurately, and the difference in heats of reaction is equal to the change.

$$\text{S (monoclinic) } (s) + O_2\ (g) = SO_2\ (g) \qquad \Delta H = -69.38 \text{ kcal}$$

$$\text{S (rhombic) } (s) + O_2\ (g) = SO_2\ (g) \qquad \Delta H = -69.30 \text{ kcal}$$

Subtracting gives

$$\text{S (monoclinic)}(s) = \text{S (rhombic)} \qquad \Delta H = -0.08 \text{ kcal}$$

As a general rule, the denser of the two forms requires more energy to pull the atoms apart, and the heat of any reaction involving this material is accordingly less, if other factors remain the same. The rhombic form is more dense at 25° than the monoclinic, and it evolves 80 cal less than does the monoclinic variety.

The molar heats of combustion are usually very large numbers so that a high order of accuracy is necessary for calculating heats of formation. These and other thermochemical data derived from them depend on differences between heats of combustion. Thus a fairly small percentage

* Rossini, *Bur. Standards J. Research*, **12**, 735 (1934); Richardson and Parks, *J. Am. Chem. Soc.*, **61**, 3543 (1939); Huffman and Ellis, *J. Am. Chem. Soc.*, **57**, 41 (1935), and later papers.

error in the heat of combustion may introduce a large error in the difference between two different substances.

Example 4. What per cent error in the calculation of the heat of formation of *n*-butane will be introduced by an error of 0.2 per cent in the heat of combustion of butane?

$$C_4H_{10}\,(g) + 6\tfrac{1}{2}O_2 = 4CO_2\,(g) + 5H_2O\,(l) \qquad \Delta H = -688.0 \text{ kcal}$$

$$\Delta H_f \text{ for } CO_2 = 4 \times (-94.0);$$

$$\Delta H_f \text{ for } H_2O = 5 \times (-68.3);$$

$$\Delta H_f \text{ for } O_2 = 0.$$

$$\Delta H_f \text{ for } n\text{-butane} = 688.0 - 376.0 - 341.5 = -29.5 \text{ kcal}$$

An error of 0.2 per cent in 688.0 is 1.38 kcal. An error of 1.38 in the heat of formation of butane is an error of 1.38/29.5 or 4.7 per cent.

If more accurate values for CO_2 and H_2O are used, -94.03 and -68.32 kcal, the value calculated for the heat of formation of *n*-butane is -29.7 kcal per mole, as in Table I.

The heats of combustion of a few substances are listed in Table II.

TABLE II

HEATS OF COMBUSTION AT CONSTANT PRESSURE

ΔH in kcal per mole at 25°

Graphite, C	−94.0	*n*-Pentene-1, C_5H_{10} (*g*)	−806.8
Diamond, C	−94.5	Cyclohexene, C_6H_{10} (*l*)	−891.0
Methane, CH_4 (*g*)	−212.8	Benzene, C_6H_6 (*l*)	−781.4
Ethane, C_2H_6 (*g*)	−372.8	Methanol, CH_3OH (*l*)	−173.7
Propane, C_3H_8 (*g*)	−530.6	Ethanol, C_2H_5OH (*l*)	−326.7
n-Butane, C_4H_{10} (*g*)	−688.0	*n*-Propanol, C_3H_7OH (*l*)	−482.2
iso-Butane, C_4H_{10} (*g*)	−686.3	*n*-Butanol, C_4H_9OH (*l*)	−638.2
n-Pentane, C_5H_{12} (*g*)	−845.3	Glycerol, $C_3H_8O_3$ (*l*)	−396.8
n-Hexane, C_6H_{14} (*l*)	−994.8	Formic acid, CH_2O_2 (*l*)	−62.8
n-Heptane, C_7H_{16} (*l*)	−1150.8	Acetic acid, $C_2H_4O_2$ (*l*)	−208.0
n-Octane, C_8H_{18} (*l*)	−1306.8	Oxalic acid, $C_2H_2O_4$ (*s*)	−59.7
Cyclohexane, C_6H_{12} (*l*)	−936.4	Succinic acid, $C_4H_6O_4$ (*s*)	−356.2
Ethylene, C_2H_4 (*g*)	−337.3	Fumaric acid, $C_4H_4O_4$ (*s*)	−318.7
Propylene, C_3H_6 (*g*)	−491.8	Maleic acid, $C_4H_4O_4$ (*s*)	−324.1
n-Butene-1, C_4H_8 (*g*)	−649.7	Benzoic acid, $C_7H_6O_2$ (*s*)	−771.5

Heats of combustion are useful in calculating other thermochemical data. Also they have practical as well as theoretical importance. The

heating value of fuel is an important matter. The purchaser of coal should be interested in its heat of combustion as well as in its weight. The dietician must know among other factors the calories obtainable from various foods.

Thermochemical Constants. Thermochemical data are necessary for many calculations of theoretical significance in the predictions of chemical equilibria and reaction rates. It will be shown on page 286, for example, that when specific heat curves of reactants and products are known down to absolute zero, then, a knowledge of the heat of reaction permits a simple and accurate calculation of the equilibrium constant of a chemical reaction. In many of these calculations the heats of reaction constitute the least satisfactory part of our available data.

In looking up thermochemical data one turns first to Bichowsky and Rossini's * critical compilation of heats of formation of inorganic compounds and the simpler organic compounds (less than four carbon atoms). If the material is not there, it may be in "International Critical Tables," Vol. V, page 169,† or possibly in the recent literature.‡ Very accurate work on heats of combustion has been done by Rossini, by Parks, and by Huffman. Heats of hydrogenation and bromination of unsaturated organic compounds have been determined accurately by Kistiakowsky § and his coworkers.

An excellent scheme for estimating heats of formation and heat capacities has been developed by Andersen, Beyer, and Watson.‖ Each compound is regarded as a fundamental group which is modified by replacing its atoms with new groups. For example, a paraffin hydrocarbon is derived from methane by successive substitutions of CH_3 groups for hydrogen atoms. Definite values of $\Delta(\Delta H_f)$ are assigned to various group replacements such as OH, C_6H_5, NH_2, Cl, and to the replacement of single bonds by multiple bonds.

If experimental data cannot be found directly or indirectly by combining several equations, one is forced to make guesses based on the heats of reaction of similar compounds for which data are available.

As a last resort one can estimate heats of reaction from data of Table III by adding a definite number of calories for each bond broken in the

* Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, 1936.

† "International Critical Tables," McGraw-Hill Book Co., New York, 1929.

‡ Rossini and associates, *Circ. Natl. Bur. Standards* C 461, Washington, D. C., 1947.

§ Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.*, **58**, 146 (1936), and other articles.

‖ Hougen and Watson, "Chemical Process Principles II," John Wiley & Sons, New York, 1947, page 758.

TABLE III

HEATS OF DISSOCIATION OF BONDS

Bond	ΔH Dissociation, kcal	Bond	ΔH Dissociation, kcal
C—C	59	H—H	103
C=C	100	Br—Br	46
C≡C	123	O—H	118
C—H	87	=N—N=	20
C—Cl	67	H—Cl	103
C—Br	54	H—I	71
C—I	45	C—O	70
O—H	110	C=O	150

reactants and subtracting a definite number for each bond formed in the products.

To illustrate the use of this table, the reaction,

$$C_2H_4 + H_2 = C_2H_6$$

may be considered; one H—H bond and one C=C bond are broken, absorbing 203 kcal, whereas one C—C bond and two new C—H bonds are formed, evolving 233 kcal. The net result is 30 kcal, which is in good agreement with the correct value of 33 kcal.

This crude method leaves little allowance for structural features such as the formation of rings and conjugated double bonds.

Kharasch * has developed a comprehensive method for estimating the heat of combustion of an organic substance from a knowledge of its molecular structure and the total number of electrons shifted in the formation of the CO_2 molecules. The agreement with experimental measurements is very good. The original article must be consulted for details.

Variation of Heat Capacity with Temperature. In the preceding chapter it was shown that the heat capacity of a monatomic gas at constant pressure is 5.0 cal per mole at all temperatures and that the heat capacity of polyatomic gases, as illustrated in Fig. 38 on page 117, are greater than this and increase with the temperature. Empirical equations giving the molar heat capacities of a number of gases as a function of temperature are recorded in Table IV.

* Kharasch, *Bur. Standards J. Research*, **2**, 359–430 (1929).

TABLE IV

MOLAR HEAT CAPACITIES OF GASES AT CONSTANT PRESSURE IN CALORIES DEGREE^{-1} MOLE^{-1}

$C_p = \Gamma_0 + \Gamma_1 T + \Gamma_2 T^2$

Gas	Γ_0	$\Gamma_1 \times 10^3$	$\Gamma_2 \times 10^6$
H_2 [3]	6.62	0.81	....
N_2 [3]	6.76	0.606	0.13
O_2 [3]	6.76	0.606	0.13
CO [3]	6.60	1.2	....
HCl [2]	6.70	0.84	...
HBr [2]	6.80	0.84	..
HI [2]	6.93	0.83	....
Cl_2 [2]	8.28	0.56	....
F_2 [3]	6.50	1.00	....
S_2 [2]	7.75	0.89	....
H_2O [2]	7.00	2.77	....
H_2O [3]	8.22	0.15	1.34
CO_2 [3]	7.70	5.3	−0.83
H_2S [2]	7.15	3.32	...
SO_2 [3]	7.70	5.30	−0.83
NH_3 [1]	6.70	6.30	.
CH_4 [1]	5.34	11.5	

[1] From 300 to 800° K.
[2] From 300 to 1500° K.
[3] From 300 to 2500° K.

These heat-capacity equations are important in many practical calculations, but data from which to determine them are very meager, particularly for the more complex molecules and at the higher temperatures. Quite recently important progress has been made in deriving them from spectroscopic data with the aid of statistical mechanics (page 690). For the simple molecules the calculations are often more accurate than the calorimetrically determined data, especially at elevated temperatures.

To calculate accurately the quantity of heat absorbed, at constant pressure when the temperature of a substance is increased, it is necessary to integrate the equation, $dH = C_p\,dT$, between the desired temperature limits.

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} C_p\,dT \qquad (2)$$

Example 5. Calculate the amount of heat required to raise a mole of carbon dioxide from 25 to 200°.

$$\int_{298.1}^{473.1} dH = \int_{298.1}^{473.1} (7.70 + 0.0053T - 0.00000083T^2)\, dT$$

$$\Delta H = H_{473.1} - H_{298.1} = 7.70(473.1 - 298.1) + \frac{0.0053}{2}(473.1^2 - 298.1^2)$$

$$- \frac{0.00000083}{3}(473.1^3 - 298.1^3)$$

$$= 1347.5 + 357.6 - 22.0 = 1683.1 \text{ cal}$$

When the temperature is limited to a narrow range or the change of heat capacity with temperature is small, it is satisfactory to use the average heat capacity rather than the integrated heat capacity. Then the heat absorbed is given by the expression:

$$\Delta H = C_{p\ \text{avg.}} \times (T_2 - T_1) \tag{3}$$

These equations for the heat capacities at constant pressure can be transformed into the corresponding equations at constant volume C_v by subtracting 1.987 from the first term, in agreement with the relation developed in the preceding chapter that $C_p - C_v = R$.

Variation of Heat of Reaction with Temperature. It has been shown that, for a mole of any substance,

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

For a chemical reaction there are two heat capacities and two enthalpies involved, one for the reactants and one for the products, thus,

$$H_{\text{products}} - H_{\text{reactants}} = \Delta H$$

and

$$C_{p\ \text{products}} - C_{p\ \text{reactants}} = \Delta C_p$$

Then, for the whole reaction,

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p \tag{4}$$

and, since the term ΔH is used for the heats of reaction *at constant pressure*, it is unnecessary to specify further the constancy of the pressure. Then, equation 4 may be written as

$$\frac{d\Delta H}{dT} = \Delta C_p \tag{5}$$

If we remember that ΔH is equal to q_p the heat of reaction at constant pressure, this equation may be stated in words as follows: *The increase*

in heat of reaction at constant pressure per degree rise in temperature is equal to the heat capacity of the products minus the heat capacity of the reactants. This differential equation can be expressed in words in this manner because one degree is such a small quantity that it may be put equal to dT.

For larger temperature differences, equation 5 must be integrated between the two temperatures, T_1 at which ΔH is ΔH_1, and a higher temperature T_2 at which ΔH is ΔH_2:

$$\Delta H_2 - \Delta H_1 = \int_{\Delta H_1}^{\Delta H_2} d\Delta H = \int_{T_1}^{T_2} \Delta C_p \, dT \tag{6}$$

If ΔC_p is practically independent of temperature, over the temperature range from T_1 to T_2, equation 6 becomes

$$\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1) \tag{7}$$

and

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p \tag{8}$$

These simple formulas 6 and 8 are very useful for calculating the heat of reaction at a given temperature when it is known at another temperature and when the heat capacities of the reactants and products are known or can be calculated.

If the heat capacity changes with temperature, it is necessary to know ΔC_p as a function of temperature, and then the heat of reaction at different temperatures can be calculated by equation 6 from standard rules of integrations as illustrated in example 6.

Example 6. Calculate the heat of combustion of hydrogen at 120° from a knowledge of the heat of reaction at 25°.

$$2H_2\,(g) + O_2\,(g) = 2H_2O\,(l) \qquad \Delta H_{298} = -136{,}600$$

Calculating ΔH for the same reaction at 100°, using the molar heat capacities for H_2 and O_2 from Table IV, and assuming that the molar heat capacity of liquid water is 18 cal throughout the whole temperature range, we find

$$\begin{aligned}
\Delta H_{373} &= \Delta H_{298} + \int_{298}^{373} \Delta C_p \, dT \\
&= \Delta H_{298} + \int_{298}^{373} [(2 \times 18) - 2 \times (6.62 + 0.81 \times 10^{-3}T) \\
&\qquad - (6.76 + 0.606 \times 10^{-3}T + 0.13 \times 10^{-6}T^2)] \, dT \\
&= -136{,}600 + 36(373 - 298) - [20.00(373 - 298) \\
&\qquad - \tfrac{1}{2}(0.002226)(373^2 - 298^2)] - \tfrac{1}{3} \times 0.13 \times 10^{-6} \times (373^3 - 298^3) \\
&= -136{,}600 + 2700 - 1500 - 56 - 1 \\
&= -135{,}457
\end{aligned}$$

At temperatures just above 100° the product is steam instead of liquid water, and sufficient heat is absorbed to vaporize the water, namely, 539.7 cal per gram.

$$2H_2O\ (l) = 2H_2O\ (g) \qquad \Delta H_{373} = 36.03 \times 539.7 = 19{,}445 \text{ cal}$$

Then

$$2H_2\ (g) + O_2\ (g) = 2H_2O\ (g) \qquad \Delta H_{373} = -135{,}457 + 19{,}445$$
$$= -116{,}012 \text{ cal}$$

Finally, for this reaction at 120°, giving steam, further calculation must be made using the molar heat capacities of steam, hydrogen, and oxygen.

$$\Delta H_{393} = \Delta H_{373} + \int_{373}^{393} [2 \times (8.22 + 0.15 \times 10^{-3}T + 1.34 \times 10^{-6}T^2)]$$
$$-[2 \times (6.62 + 0.81 \times 10^{-3}T)$$
$$+ (6.76 + 0.606 \times 10^{-3}T + 0.13 \times 10^{-6}T^2)]\, dT$$
$$= -116{,}091 \text{ cal}$$

REFERENCES

Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, 1936.

Wenner, "Thermochemical Calculations," McGraw-Hill Book Co., New York, 1941.

Daniels, Mathews, and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1941.

Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

"International Critical Tables," McGraw-Hill Book Co., New York, 1929.

Parks and Huffman, "Free Energy of Some Organic Compounds," Reinhold Publishing Corp., New York, 1932.

Hougen and Watson, "Chemical Process Principles II," John Wiley & Sons, New York, 1947.

Rossini, Pitzer, Taylor, Ebert, Kilpatrick, Rackett, Williams, and Werner, "Selected Values of Properties of Hydrocarbons," *Circ. Natl. Bur. Standards* C 461, Washington, D. C., 1947.

PROBLEMS

1. Compute the heat of reaction per mole of lead, in the smelting of lead,

$$PbS + O_2 = Pb + SO_2$$

from the data on the heats of formation and the equations,

(*a*) $PbS + 2O_2 = PbSO_4$ and $PbSO_4 + PbS = 2Pb + 2SO_2$

Check the calculation, using the equations,

(*b*) $2PbS + 3O_2 = 2PbO + 2SO_2$ and $2PbO + PbS = 3Pb + SO_2$

Ans. $\Delta H = -48.6$ kcal.

2. In an adiabatic calorimeter, the combustion of 1.6324 g of sucrose produces a temperature rise of 2.854°. The molar heat of combustion of sucrose is 1349.6 kcal.

(*a*) What is the total heat capacity of the water and the calorimeter?

(*b*) If the calorimeter contains 1850 g of water (specific heat = 1.0), what is the effective heat capacity of the calorimeter? In this problem, corrections for the oxidation of the wire and residual nitrogen may be neglected.

Ans. (*b*) 405 cal deg.$^{-1}$

3. For acetone ΔH_f is -61.4 kcal at 25°.

(*a*) Calculate the heat of combustion at constant pressure.

(*b*) Calculate the heat evolved when 2 g of acetone is burnt under pressure in a closed bomb at 25°. *Ans.* (*a*) 426 kcal. (*b*) 14.6 kcal.

4. For the compound $CHClF_2$,

$$C_v = 10.44 + 0.0230t$$

where C_v = calories per (mole) (°C)

t = °C

This relationship holds from 35 to 135°. Calculate the change in internal energy ΔE of the gas in going from 35 to 135°. *Ans.* 1239 cal per mole.

5. Calculate the heat evolved in the reaction $H_2 + Cl_2 = 2HCl$ at 1023° and constant pressure. *Ans.* -45.5 kcal.

6. From the table of the heats of formation calculate the heats of combustion at constant pressure at 25° of (*a*) CO, (*b*) H_2, (*c*) C_2H_6, and (*d*) C_2H_5OH.

7. (*a*) Calculate the heat of formation of PCl_5 (*s*), given the heats of the following reactions at 25°.

$$2P\ (s) + 3Cl_2\ (g) = 2PCl_3\ (l) \qquad \Delta H = -151{,}800 \text{ cal}$$

$$PCl_3\ (l) + Cl_2\ (g) = PCl_5\ (s) \qquad \Delta H = -32{,}810 \text{ cal}$$

(*b*) State precisely what data would be needed to calculate the heat of formation of PCl_5 (*s*) at some other temperature.

8. The heat of formation of nitric oxide from nitrogen and oxygen has been calculated from spectroscopic data. A direct calorimetric determination is desirable, however. It has been found that phosphorus will burn completely to P_2O_5 in nitric oxide leaving nitrogen, if the phosphorus is thoroughly ignited with a hot arc. Calculate the heat of formation of NO from the following data.

Phosphorus was burnt in a calorimeter in a stream of nitric oxide for 12.00 min and produced 1.508 g H_3PO_4. The calorimeter was surrounded by 1386 g of water. The observed temperature rise was 2.222°, and the cooling correction amounted to 0.037°. The correction for the heat of stirring was 11.1 cal evolved per minute. The heat capacity of the calorimeter, as determined with an electric heater, was 244 cal per degree.

The same experiment was repeated in which the nitric oxide was replaced by a mixture of half nitrogen and half oxygen. The measurements were then repeated. The amount of H_3PO_4 produced was 2.123 g. Time 10.00 min. Observed temperature rise 2.398°. Cooling correction 0.032. Correction for heat of stirring 12.2 cal per minute. Weight of water 1386 g. Heat capacity of calorimeter 244 cal per degree. What is the heat of formation of NO?

9. The heat of combustion at constant pressure and 25° of liquid carbon disulfide CS_2 is 246.6 kcal per mole. (*a*) Calculate the heat of combustion per mole at constant volume in a closed bomb. (*b*) Calculate the heat of formation ΔH_f of liquid carbon disulfide.

10. (*a*) From the table of heats of formation calculate the heat of complete combustion of butanol at constant pressure at 25°. (*b*) Calculate the heat of combustion at constant volume. (*c*) Estimate the heat of combustion ΔH from the bond energies.

11. The equation for the molar heat capacity of *n*-butane is

$$C_p = 4.64 + 0.0558T$$

Calculate the heat necessary to raise the temperature of one mole from 25 to 300°.

12. $H_2O\,(g) + C \rightarrow CO + H_2 \qquad \Delta H = 31{,}404$ cal at 25°

$$C_p(H_2O) = 7.00 + 0.00277T$$
$$C_p(C) = 2.673 + 0.002617T - \frac{1.169 \times 10^5}{T^2}$$
$$C_p(CO) = 6.60 + 0.00120T$$
$$C_p(H_2) = 6.62 + 0.00081T$$

Calculate ΔH at 400°.

13. Estimate the molal heat of combustion ΔH of *n*-nonane, C_9H_{20}, from the data on octane, heptane, and hexane.

---

14. Calculate the heat evolved at 25° in the reaction $3Mg + Fe_2O_3 \rightarrow 3MgO + 2Fe$. When magnesium is oxidized to MgO, $\Delta H = -145{,}700$ cal. Show that, in measuring the isothermal heat of a reaction, no error is introduced if the temperature rises, provided that the products are cooled to the original temperature of the reactants.

15. In an adiabatic calorimeter, 0.4362 g of naphthalene caused a rise of 1.707° in temperature. The heat capacity of the calorimeter and water was 2460 cal per degree. If corrections for the wire and residual nitrogen are neglected, what is the heat of combustion of naphthalene per mole?

16. (*a*) Calculate the heat evolved when 1 g of ethylene is exploded at constant pressure at 25° with an excess of air.

(*b*) Calculate the heat evolved when 1 g of ethylene is exploded with an excess of pure oxygen at 20 atm pressure in a closed bomb.

17. One hundred grams of iron is dissolved in dilute acid at 25° giving a ferrous salt. Will more heat be evolved when the reaction is carried out in an open beaker or in a closed bomb? How much more?

18. (*a*) Estimate from heats of formation and bond energies the heat of dissociation of HBr gas into atoms.

(*b*) Estimate the heats of the following reactions at constant pressure assuming that all reactants and products are in the gaseous state:

$$C_2H_4 + Br_2 = C_2H_4Br_2$$

$$C_2H_6 + 2Br_2 = C_2H_4Br_2 + 2HBr$$

19. For methane $C_p = 5.34 + 0.0115T$. With this fact and data from this chapter, calculate $\Delta H_{1000°}$ for the reaction $CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$.

20. Calculate the molar heat of combustion of carbon monoxide at constant pressure and 1327°.

21. As a rough approximation, the molar heat capacity of a *solid* is of the same order of magnitude as the sum of the atomic heat capacities of the solid elements of

which the solid compound is formed. What general statement can be made regarding the influence of temperature on the heat of reactions of solids to give solids, as, for example, the reaction Fe + S = FeS?

22. One British thermal unit (Btu) is the heat required to raise the temperature of 1 lb of water 1° F. Calculate the number of British thermal units evolved by the complete combustion at constant pressure and 25° of 1 cu ft of water gas ($\frac{1}{2}$ CO and $\frac{1}{2}$ H_2 by volume) measured at 25° and 1 atm.

23. For the following reaction $\Delta H = 47.16$ kcal:

$$CH_3COONa\ (aq) = CH_2CO\ (g) + NaOH\ (aq)$$

Calculate the heat of formation of ketene, CH_2CO (g), obtaining additional data from tables of thermochemical data.

24. How many grams of cane sugar ($C_{12}H_{22}O_{11}$) must be oxidized to give the same number of calories of heat as the number of calories of work done by a 160-lb (59.8-kg) man in climbing a mountain 1 mile (1.609 km) high? The heat of combustion of $C_{12}H_{22}O_{11}$ is 1349.7 kcal per mole.

25. In some of the published tables of heats of formation and other thermodynamic properties diamond is taken as the standard state of carbon instead of graphite. Derive a relation between the heats of formation based on these two choices of the standard state of carbon, for a substance containing n carbon atoms per mole.

CHAPTER VIII

THERMODYNAMICS

The Second Law of Thermodynamics. Although work can always be transformed into heat, it does not follow that heat can be transformed completely into work. The first law of thermodynamics given on page 101 merely specifies that, when heat is converted into work, a definite quantitative relationship exists between the heat converted and the work done, but it tells nothing as to the maximum amount of work which can be obtained from a given quantity of heat. The second law of thermodynamics gives information as to the limitations which experience has shown govern the transformation of heat into work. It states that heat cannot pass from a colder to a hotter body unless work is supplied from an outside source. In general, heat can pass spontaneously only from a higher temperature to a lower temperature just as a body of water can flow only from a higher level to a lower level. Again, an engine operating in a cycle can do work only when there is a transfer of heat from a higher to a lower temperature.

A kinetic explanation is helpful. If one end of a tube of gas is hot and the other end cold, heat will flow from the hot end to the cold and in so doing could do work. But after the motions of molecules have become averaged throughout, and the whole tube is at a uniform temperature, it is extremely improbable that the more rapidly moving molecules would all move spontaneously to one end, causing the tube to become hot at one end and cold at the other. In fact, it is far less likely than that a pack of cards after being shuffled should, by continued shuffling, return to the original order. It is less likely because the number of molecules is much greater than the number of cards in a pack, and the laws of probability hold better when large numbers are involved.

The second law of thermodynamics may be applied to a variety of phenomena. It may be stated in a more general way as follows: *All systems tend to approach a state of equilibrium.* The natural movement of heat from a high temperature to a lower temperature and the impossibility of a spontaneous movement of heat from a low to a higher temperature have been cited. The movement of molecules of a dissolved substance from a region of high concentration to a region of low concentration giving uniform concentration throughout the whole solution

is another manifestation of the second law. The running down of a clock or the reaction of zinc and sulfuric acid are other illustrations.

The second law is statistical, and like all statistical laws it breaks down when only a small number of individuals is involved. For example, if there are more small particles moving around on one side of a microscopic field than on the other side, the general tendency is for particles to migrate from the region of high concentration to the region of low concentration until the concentration is uniform throughout, but occasionally it will be observed that a particle moves in the opposite direction making the low concentration still lower, contrary to the prediction. When there is a large number of particles, this occasional movement against the general traffic becomes comparatively rarer.

Entropy.* In order to express the second law in concise mathematical form, it is helpful to introduce the concept of entropy.* Entropy, designated by the symbol S, is helpful in thermodynamical calculations of such quantities as engine efficiencies and chemical equilibria. The entropy of a system, like internal energy E, or enthalpy H, is characteristic of the state of the material and does not depend on the previous history of the system. A change in entropy ΔS, or $S_2 - S_1$, depends only on the initial and final states. The amount of work done w and the heat absorbed q may change, depending on how the experiment is carried out, but ΔS will always be the same, provided only that the initial and final states are the same. The change in entropy of a system (dS) for an infinitesimal, *reversible* process is defined by the equation,

$$dS = \frac{dq_{\text{rev.}}}{T} \tag{1}$$

where $dq_{\text{rev.}}$ is the heat absorbed from the surroundings. For any *natural* process complete reversibility can never be attained on account of such effects as frictional losses which accompany practical operations. Then the entropy change of the system is greater than the heat absorbed, from the surroundings, divided by the absolute temperature; thus,

$$dS > \frac{dq}{T} \tag{2}$$

The change in entropy of a given process may be defined as the heat absorbed divided by the absolute temperature under conditions such that the process is always reversible.

If a process is irreversible, then, in order to calculate the entropy change, it is necessary to devise a means of passing from the same initial

* En'tropy is accented on the first syllable.

state to the same final state by a series of isothermal reversible processes and measuring the heat absorbed in each step. For example, a mole of gas at 10 atm pressure at 25° might be expanded to a larger volume at 1 atm at 25° by reducing the pressure to 1 atm in a single step. The heat absorbed would not be a measure of the entropy change because the process is not reversible. The process can be carried out reversibly, however, by expanding against a constantly decreasing pressure which is always slightly less than the pressure of the gas itself. Under these conditions the process is reversible, and the heat absorbed is a correct measure of the entropy increase which accompanies the expansion of the gas. Frequently, in order for the process to be reversible, the steps must be infinitesimally small steps, and the total entropy change is then obtained by integration.

According to the second law of thermodynamics, all systems tend to approach a state of equilibrium, and entropy can be used as a quantitative measure of the extent to which this equilibrium has been approached. Consider first an isolated system, thermally insulated so that $dq = 0$. If the process is reversible, that is, in a state of equilibrium, it follows from equation 1 that $ds = dq/T$, and, since $dq = 0$,

$$dS = 0 \tag{3}$$

If the system is not in a state of equilibrium and the process is not reversible, equation 2 is applicable, and, since dq is still zero in this isolated system,

$$dS > 0 \tag{4}$$

The more nearly reversible the process is, the closer will dS approach zero. The increase in entropy which accompanies a process taking place in an isolated system may thus be considered a measure of the approach of the system to a state of equilibrium.

From a slightly different point of view, the entropy of a system may then be regarded as a function of the probability of the thermodynamic state, the state of equilibrium being the most probable; and the tendency for the entropy of an isolated system to increase corresponds to the tendency of the system, if left alone, to go to a state of higher probability, that is, to equilibrium. This idea leads to another general definition according to which *entropy is a measure of the disorder of a system*. The more the molecules in a system are distributed in a disordered or random manner, the more probable is the arrangement, and the greater is the entropy. The greater the entropy, the smaller is the entropy increase required to bring the system to the state of maximum entropy which exists in the disordered state of complete equilibrium.

Entropy Calculations. A few concrete examples of entropy calculations will now be offered. The transfer of heat from one body to another at constant temperature is a reversible process if the direction of heat flow may be reversed by infinitesimal changes in the temperature of one of the bodies. The fusion of a solid at its melting point or the evaporation of a liquid at a constant pressure equal to its vapor pressure are examples of isothermal reversible processes in which the entropy change is readily visualized and easily calculated. Integration of equation 1 yields, when T is constant,

$$S_2 - S_1 = \Delta S = \frac{q_{\text{rev.}}}{T} \tag{5}$$

Example 1. Solid mercury melts at $-38.9°$ C with the absorption of 560 cal per mole. The process is isothermal, and the melting may be easily reversed by lowering the temperature of the surroundings infinitesimally; so the process must be reversible.

$$\text{Hg } (s) \longrightarrow \text{Hg } (l)$$

$$\Delta S = \frac{q_{\text{rev.}}}{T} = \frac{560}{234.2} = 2.39 \text{ cal per degree} = 2.39 \text{ entropy units}$$

The molal entropy of a liquid is always greater than that of the solid at the freezing point.

Entropy has the dimensions of energy divided by absolute temperature, and the usual entropy units are given in calories per degree.

The entropy increase involved in raising the temperature of a substance may be calculated also. The heat absorbed is equal to the heat capacity C multiplied by the increase in temperature, and, if the changes are kept infinitesimally small, the process is reversible. Thus,

$$dq_{\text{rev.}} = C\,dT$$

and

$$dS = \frac{dq_{\text{rev.}}}{T} = \frac{C\,dT}{T} \tag{6}$$

As the temperature is raised, each infinitesimal absorption of heat must be divided by the temperature at which the absorption takes place, a calculation which is readily made with the help of calculus. Integrating between the limits T_1 and T_2 gives

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \frac{C\,dT}{T} \tag{7}$$

If C is constant,

$$S_2 - S_1 = C\,(\ln T_2 - \ln T_1) = C \ln \frac{T_2}{T_1} = 2.303C \log \frac{T_2}{T_1} \tag{8}$$

This formula is equally applicable for constant pressure or constant volume. If the heating is carried out at constant pressure, C_p is used, and, if it involves constant volume, C_v is used. Chemical operations usually involve constant pressure.

Example 2. Calculate the increase in entropy involved in heating a mole of liquid mercury at constant pressure from 234.2 to 298.1° K. The average molal heat capacity at constant pressure over this temperature is 6.70 cal per degree.

$$\Delta S = S_2 - S_1 = 2.303 \times 6.70 \log \frac{298.1}{234.2} = 1.71 \text{ cal per degree}$$

Example 3. When a mole of supercooled water freezes isothermally at −10° C, what is the change in entropy? The process is irreversible. In order to calculate the entropy change, the process must be carried out in steps, every one of which is reversible, and the absorption or evolution of heat must then be measured in each reversible step. Thus,

$$H_2O\ (l) \text{ at } -10° \rightarrow H_2O\ (l) \text{ at } 0° \qquad \Delta S = \int_{-10°}^{0°} C_{\text{liq.}} \frac{dT}{T}$$

$$H_2O\ (l) \text{ at } 0° \rightarrow H_2O\ (s) \text{ at } 0° \qquad \Delta S = \frac{q_{\text{rev.}}}{T}$$

$$H_2O\ (s) \text{ at } 0° \rightarrow H_2O\ (s) \text{ at } -10° \qquad \Delta S = \int_{0°}^{-10°} C_{\text{ice}} \frac{dT}{T}$$

The crystallization of liquid water at 0° C evolves 80 × 18 cal. The specific heat of water is 1.0 cal per degree and that of ice is 0.5 cal per degree over this range. Then

$$\Delta S = \left(18 \times 1.0 \times 2.303 \log \frac{273}{263}\right) + \left(18 \times \frac{-80}{273}\right) + \left(18 \times 0.5 \times 2.303 \log \frac{263}{273}\right)$$

$$= 0.67 - 5.28 - 0.34$$

$$= -4.95 \text{ cal per degree}$$

The Third Law of Thermodynamics. The most orderly arrangement which one can think of is a crystal, with its symmetrical lattice, at absolute zero where random motions due to thermal agitation have ceased. Here the entropy should be very small, and, in fact, according to the *third law of thermodynamics*, the *entropy of most crystals may be taken as zero at the absolute zero.*

There is as yet no direct, conclusive proof of the validity of the third law, but it has been checked and cross-checked in many different ways. It is important because it makes possible the determination of the absolute entropies of chemical compounds and the calculation of chemical equilibria, as is explained on page 286. The idea on which the third law is based was first proposed by T. W. Richards in 1902. The law was

propounded by Nernst and fully developed and applied to chemical problems by G. N. Lewis and his associates and others.*

In calculating entropy, the entropy is taken as zero at the absolute zero; as the temperature rises, the molecules and parts of molecules absorb heat and move in a random manner. The higher the temperature, the greater is the disordered motion, the greater is the amount of heat which has been absorbed, and the greater is the entropy of the substance. This concept of entropy can be made quantitative as well as qualitative. The increase in entropy involved in heating from absolute zero to any specified temperature may be calculated with the help of equation 9,

$$S = \int_0^T C \, d \ln T \tag{9}$$

and, according to the third law, this increase in entropy is the absolute entropy. Tables of entropy have been prepared from specific heat data, and from these entropies the entropy changes in chemical reactions can be determined from the relation $\Delta S = S_{\text{products}} - S_{\text{reactants}}$.

The determination of entropies is illustrated with the data on silver shown in part in Table I and plotted in **Fig. 40.**

If the entropy is taken at 0° K as zero, according to the third law, and equation 9 is applied, the entropy at 298.1° K is given by the equation:

$$S_{298} = 2.303 \int_0^{298.1\text{ K}} C \, d \log T \tag{10}$$

The theoretical relation between C and log T is not known (except at very low temperatures), and so it is necessary to evaluate the integral by graphical means. The area $\left(\int y \, dx\right)$ is determined by plotting accurately C_v against log T and counting the squares under the curve out to log 298.1° K, this area in turn being multiplied by the conversion factor of natural logarithms. For silver, the value of $S_{298.1\text{ K}}$ obtained by evaluating this area is 10.21 entropy units (calories per degree).

Specific heat measurements have been made with special electric calorimeters on many substances down to liquid-air temperatures, and on some substances down to the boiling point of hydrogen, and lower.

* Lewis, Gibson, and Latimer, *J. Am. Chem. Soc.*, **44,** 1008 (1922); Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923; Parks and coworkers, *J. Am. Chem. Soc.*, **47,** 338 (1925); **48,** 1506, 2788 (1926); **52,** 1032, 1547, 3241, 4381 (1930); and later articles; Giauque and Blue, *J. Am. Chem. Soc.*, **58,** 831 (1936); Aston, in Taylor and Glasstone, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1942, Chapter IV.

The extrapolation to absolute zero does not involve very large errors, and, fortunately, in the region of absolute zero, the specific heat–temperature curve can be calculated with fair accuracy (p. 119).

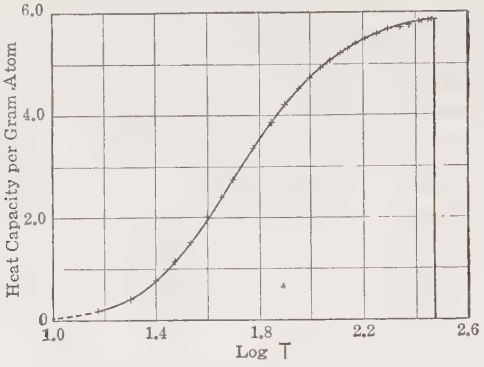


FIG. 40. Graph for calculating absolute entropy of silver from heat capacity to absolute zero.

TABLE I

HEAT CAPACITY OF SILVER [1]

T	Log T	C_v	T	Log T	C_v
15	1.1761	0.160	140	2.1461	5.310
20	1.3010	0.410	160	2.2041	5.461
25	1.3979	0.747	180	2.2553	5.584
30	1.4771	1.140	200	2.3010	5.653
40	1.6021	2.001	220	2.3424	5.708
60	1.7782	3.405	240	2.3802	5.765
80	1.9031	4.245	260	2.4150	5.819
100	2.0000	4.769	280	2.4472	5.843
120	2.0792	5.092	298.1	2.4744	5.851
			300	2.4771	5.852

[1] Meads, Forsythe, and Giauque, *J. Am. Chem. Soc.*, **63**, 1902 (1941).

An increase in entropy is produced by mixing two substances, and, if the entropy of these pure substances is zero at 0° K, the mixture cannot be zero also. Accordingly, the third law is restricted to pure crystals, but often it may be applied, with only small errors,* to solutions and glasses.

* An interesting case is that of hydrogen, which exists in two forms, ortho and para, having different specific heats as described in Chapter XIX. Thermodynamical

If there is a change of state, or a transition from one crystalline form to another, the heat absorbed in the change must be divided by the temperature at which the change takes place, and added to the entropy as calculated from the specific-heat curve.

Table II gives the entropies at constant pressure of 1 atm for a number of elements and compounds obtained from these specific-heat measurements at low temperatures. Data of this type can be used in the calculation of chemical equilibria as shown in Chapter XII.

TABLE II

Atomic and Molecular Entropies at 25°

Water (*l*)	16.8	Methane (*g*)	44.5
Hydrogen ($\frac{1}{2}H_2$) (*g*)	15.6	Methanol (*l*)	30.3
Carbon (diamond)	0.6	Maleic acid (*s*)	38.1
Carbon (graphite)	1.4	Fumaric acid (*s*)	39.7
Nitrogen ($\frac{1}{2}N_2$)	22.9	Benzene (*l*)	41.9
Oxygen ($\frac{1}{2}O_2$)	24.5	Ethanol (*l*)	38.4
Helium (He)	29.8	*tertiary*-Butanol (*l*)	45.3
Sulfur (rhombic)	7.6	*cyclo*-Hexane (*l*)	49.2
Sulfur (monoclinic)	7.8	Toluene (*l*)	52.4
Chlorine ($\frac{1}{2}Cl_2$) (*g*)	26.6	*n*-Butanol (*l*)	54.5
Silver (*s*)	10.2	*n*-Hexane (*l*)	70.6
Mercury (*l*)	17.8	Ethylbenzene (*l*)	61.2
Hydrochloric acid (*g*)	44.7	Ethyl ether (*l*)	60.5
Carbon dioxide (*g*)	51.1	*n*-Heptane (*l*)	78.6
Copper (*s*)	8.0	Ethylene (*g*)	52.5
Lead (*s*)	15.5	Acetylene (*g*)	48.0

Free Energy and Work Content. Two other thermodynamic functions, work content A and free energy F, have been invented, in addition to internal energy E, enthalpy H and entropy S, for convenience in studying processes at constant temperature. The work content and free energy * of a phase are defined by the equations:

$$A = E - TS \tag{11}$$

$$F = H - TS \tag{12}$$

Like entropy F and A depend only on the state of the system.

---

calculations persisted in showing that the entropy of hydrogen was too low by an appreciable amount, and it is now known that an entropy increase of this magnitude due to the change from one form to the other does actually occur just above the absolute zero. The change comes at such a low temperature in the case of hydrogen that it was missed in the early experimental measurements.

*This function, called free energy and given the symbol F by G. N. Lewis, was given the symbol ζ by Willard Gibbs. It is now frequently given the symbol G.

Of these concepts free energy is perhaps the most useful in its application to chemical problems because it provides a convenient quantitative measure of the extent to which substances react chemically. It permits the calculation of chemical equilibria, as explained on page 268. The practical importance of equation 12 in such calculations is discussed on page 286.

Using the definition of H, we have

$$H = E + pv \tag{13}$$

We see that

$$F = E + pv - TS \tag{14}$$

and, further, from equation 11, we obtain the relation:

$$F = A + pv \tag{15}$$

The absolute values of A and F, like those of E and H, are not known. We are concerned, however, only with the changes in these quantities, and, in passing from the initial to the final state, we may write, for example,

$$A_2 - A_1 = E_2 - E_1 - (T_2S_2 - T_1S_1)$$

or

$$\Delta A = \Delta E - \Delta(TS) \tag{16}$$

Again

$$\Delta F = \Delta H - \Delta(TS) \tag{17}$$

and

$$\Delta F = \Delta A + \Delta(pv) \tag{18}$$

These equations are more useful under certain specific restrictions; thus, at constant temperature,

$$A_2 - A_1 = E_2 - E_1 - (TS_2 - TS_1)$$

and equation 16 becomes

$$\Delta A = \Delta E - T\,\Delta S \tag{19}$$

At constant temperature equation 17 becomes

$$\Delta F = \Delta H - T\,\Delta S \tag{20}$$

and at constant pressure equation 18 becomes

$$\Delta F = \Delta A + p\,\Delta v \tag{21}$$

Of these last six equations which follow at once from the definitions of A, F, and H, equations 20 and 21 are most frequently used in physical chemistry.

For changes at constant temperature ΔA has a physical meaning which is easy to grasp. If we consider a process which is reversible as well as isothermal,

$$T\,\Delta S = q_{\text{rev.}}$$

Substituting into equation 19 gives

$$\Delta A = \Delta E - q_{\text{rev.}}$$

By the first law of thermodynamics,

$$\Delta E - q = -w$$

and so

$$-\Delta A = w_{\text{max.}} \tag{22}$$

The work w is restricted to maximum work $w_{\text{max.}}$ because the heat q was restricted to heat in a reversible cycle $q_{\text{rev.}}$ It must be constantly born in mind that ΔA refers to the initial and final states and that its value does not depend on the manner in which the change was carried out. Only if the process is reversible, will the maximum work be done. If the process is not reversible, ΔA will still be the same, but w will be less than $w_{\text{max.}}$.

In words, the decrease in work content, as its name implies, equals the maximum amount of work which can be obtained isothermally.

The significance of ΔF at constant temperature and pressure, where it is most useful, can be seen easily from equations 21 and 22. Combining gives

$$-\Delta F = w_{\text{max.}} - p\,\Delta v \tag{23}$$

Since $p\,\Delta v$ is the work of expansion, this equation states that, *if the temperature and pressure are kept constant, the decrease in free energy equals the maximum available work other than expansion work*, that is, other than the work involved in increasing the volume of the system against a resisting pressure.

It may be worth while now to bring together three important relations between the thermodynamic quantities and to attempt descriptions in words, which, although inadequate and oversimplified, may be helpful in remembering the formulas.

According to definition in equation 13,

$$\Delta H = \Delta E + \Delta(pv)$$

The change of enthalpy is composed of two quantities, a change in the internal energy (which may be regarded roughly as the total chemical energy) plus the change in the product pv (which under the special conditions of constant pressure may be regarded as external work against the surroundings).

According to equation 17,

$$\Delta H = \Delta F + \Delta(TS)$$

The change of enthalpy is also composed of two other quantities, the change in free energy (which at constant temperature may be regarded as maximum available work excluding external pressure–volume work) plus the change in the product TS (which at constant temperature is not readily available for doing useful work). At constant temperature the term $T\,\Delta S$ is visualized as heat absorbed when the process is carried out reversibly.

According to equation 18,

$$\Delta F = \Delta A + \Delta(pv)$$

The change in free energy (which at constant temperature may be regarded as maximum available work excluding pressure–volume work) is equal to the change in work content (which may be regarded as a measure of the maximum work obtainable at constant temperature) plus the change in the product pv (which for the special case of constant pressure can be visualized as the pressure–volume work).

Influence of Pressure on Free Energy. For any infinitesimal change we obtain, by differentiation of equation 15,

$$dF = dA + p\,dv + v\,dp \tag{24}$$

If the process is reversible and isothermal, and the work restricted to that due to volume changes, we obtain, from equation 22,

$$dA = -dw_{\text{max.}} = -p\,dv \tag{25}$$

Adding equations 24 and 25 gives

$$dF = v\,dp \tag{26}$$

and

$$\left(\frac{\partial F}{\partial p}\right)_T = v$$

or, in words, at constant temperature, the rate of change of free energy with pressure equals the volume. If the system is an ideal gas, integration of equation 26 at constant temperature gives

$$\int dF = \int \frac{nRT}{p}\,dp$$

$$F = nRT \ln p + \text{constant} \tag{27}$$

or integrating between limits, F_1 and p_1 being the initial values and F_2 and p_2 being the final values,

$$\Delta F = F_2 - F_1 = nRT \ln \frac{p_2}{p_1} \tag{28}$$

This equation which is limited to process with ideal gases at constant temperature will be found useful in later chapters.

If the system is not a gas but a liquid or solid which remains constant in volume over moderate changes in pressure, we have, by the integration of equation 26,

$$\Delta F = F_2 - F_1 = v(p_2 - p_1) \tag{29}$$

This equation too will find later application.

Since the free energy depends only on the state of the system, these equations can be applied to the change from a given initial state to a given final state, even if the process originally under consideration was irreversible.

Application to a Chemical Reaction. The chemical significance of enthalpy, free energy, and entropy may be illustrated with the reaction by which copper is precipitated from a solution of copper sulfate by the addition of zinc under conditions of constant temperature and constant atmospheric pressure. The reaction is

$$Zn + Cu^{++} \rightarrow Zn^{++} + Cu$$

The change in *enthalpy* may be obtained by simply measuring the heat evolved when zinc is added to an open calorimeter containing the copper sulfate. The rise in temperature multiplied by the heat capacity of the solution and calorimeter gives directly $-q_p$ or $-\Delta H$.

The change in *free energy* may be obtained by carrying out the reaction in an electric cell made by dipping a zinc rod into a solution of zinc sulfate and a copper rod into a solution of copper sulfate and connecting the two solutions with a tube of solution or a porous plate. This little battery will operate a motor and do work which can be measured, but the maximum work obtainable is determined more accurately with a potentiometer and galvanometer (as described on page 437) under conditions such that the voltage is measured when very little current is flowing. Zinc is consumed and copper deposited by the operation of the cell, but by increasing the applied voltage slightly above the voltage of the cell, the cell may be operated backwards so that copper is consumed and zinc deposited. In other words, the process can be reversed by infinitesimal changes, and, hence, this is a way in which the reaction can be carried out reversibly. Then, by equation 23, the electrical work

measured under these conditions equals the change in free energy ($-\Delta F$). The expansion work $p\ \Delta v$, owing to the change in volume of the solution when the reaction occurs, is not measured by the potentiometer. The change in work content ($-\Delta A$) for the reaction, according to equation 22 is equal to the electrical work plus the $p\ \Delta v$ work.

As a matter of fact, in this particular reaction where no gas is involved and the change in volume of the solutions is negligibly small, the external pressure–volume work is negligible, and $\Delta F = \Delta A = -w_{\text{max.}}$ In a zinc–hydrogen cell, however, in which a mole of hydrogen gas is evolved for each mole of zinc consumed, ΔA would exceed ΔF by an energy of $p\Delta v$ or RT.

The change in *entropy* (ΔS) when zinc is added to a solution of copper sulfate in a calorimeter cannot be determined by dividing the heat of reaction by the absolute temperature, because the reaction carried out in this way is not reversible. Only reversible processes can be used in the calculation of entropy by equation 5. It is necessary to measure the heat evolved or absorbed when the reaction is carried out reversibly. For example, the zinc–copper battery just described theoretically can be placed in a calorimeter, and the heat which is evolved or absorbed can be measured while the cell is operating reversibly. Under these conditions of complete reversibility, the current drawn from the cell is so small that the calorimetric measurement would be inaccurate. As in many other deductions of thermodynamics, however, useful information can be obtained from hypothetical experiments which cannot be carried out in the laboratory.

This quantity of heat absorbed during this hypothetical operation of the cell, divided by the absolute temperature, gives the entropy change which accompanies the reaction,

$$\text{Zn} + \text{Cu}^{++} \rightarrow \text{Zn}^{++} + \text{Cu}$$

no matter how it is carried out, for ΔS depends only on the initial and final states. If a considerable current is drawn from the battery so that the process is not reversible, the work will be less than the maximum, and the heat absorbed will be less than for the reversible case. This latter statement follows from equation 2, which on integration becomes

$$\Delta S > \frac{q}{T} \tag{30}$$

for an irreversible isothermal process. However, although q will be less than $q_{\text{rev.}}$, ΔS and ΔF will be the same as calculated for the reversible cell because they depend only on the initial and final states.

Spontaneous Changes. The second law affords criteria for equilibrium and for deciding whether or not a process can possibly take place of itself. Thus, by equation 2, if $dS > dq/T$, the process is a natural one, that is, it is possible for it to take place spontaneously. If $dS = dq_{rev.}/T$, the process is reversible, or, in other words, the system is in a state of equilibrium. In adiabatic processes which involve a system *isolated from its surroundings*, $q = 0$, and the conditions are somewhat simpler: $dS > 0$ for spontaneous changes, and $dS = 0$ for changes taking place at equilibrium; while $dS < 0$ for changes which are not possible unless energy is supplied from some other source.*

For a system which is not isolated but is kept in contact with its environment at constant temperature and pressure, the free energy provides a more convenient thermodynamic criterion for equilibrium and for natural changes. These are the conditions under which many chemical processes are carried out, and, hence, free energy is very important in physical chemistry. We may start with the equation,

$$F = E + pv - TS \tag{31}$$

At constant temperature and pressure,

$$\Delta F = \Delta E + p\,\Delta v - T\,\Delta S \tag{32}$$

From equation 1,

$$q = T\,\Delta S \tag{33}$$

in reversible processes at constant temperature. By the first law of thermodynamics,

$$\Delta E = q - w \tag{34}$$

and, hence, on combining equations 32, 33, and 34, we obtain

$$\Delta F = -w + p\,\Delta v \tag{35}$$

For systems subjected to no external forces other than pressure, equation 35 simplifies to

$$\Delta F = 0 \tag{36}$$

because, under these conditions, the only work done is the pressure–volume work. According to this equation, at constant temperature and pressure, *if there is no change in free energy, the system is in a state of equilibrium.*

* It may be recalled that in example 3 the *isothermal* freezing of supercooled water at $-10°$ is accompanied by a decrease in entropy. But in this case the system is not isolated. If the supercooled water were isolated thermally in a vacuum bottle, it would not change completely into ice.

For spontaneous irreversible processes, a similar line of reasoning may be followed, starting with equation 2,

$$q < T\,\Delta S$$

and leading to the relation that

$$\Delta F < 0$$

Thus, at constant temperature and constant pressure, if ΔF has a negative value, the system can change naturally by itself. If it is a chemically reacting system, the chemical reaction can take place spontaneously.

In case $\Delta F > 0$, the system is not in a state of equilibrium, and the process will not take place spontaneously. It is evident that the reverse process would take place spontaneously, however, since for the reverse process ΔF would be less than zero.

These considerations of free energy as a criterion for equilibrium or spontaneous reaction can be illustrated with a mixture of ice and water. Both ice and water have the same free energy per mole at 0° and 1 atm pressure, and there is no tendency for the ice to melt or the water to freeze in a mixture at 0° and 1 atm. On the other hand, the free energy of water supercooled to −10° C is higher per mole than that of ice at −10°, both being under a pressure of 1 atm. The change of water to ice at this temperature and pressure is accompanied by a decrease in free energy, and, hence, it is a natural change. The change in the reverse direction, that is, ice changing to water at −10°, cannot take place spontaneously because there would then be an increase in free energy, that is, $\Delta F > 0$.

If the processes are carried out at constant volume instead of at constant pressure, the work content is a more useful thermodynamic quantity, and, by reasoning similar to that already outlined, the criterion for an equilibrium process is that

$$\Delta A = 0$$

and, for a spontaneous process, that

$$\Delta A < 0$$

These several relations are summarized in Table III

Although these criteria may show that a certain process is a natural or spontaneous one, it does not necessarily follow that the process will take place with an appreciable speed. Thus, a mixture of 1 mole of carbon and 1 mole of oxygen at 1 atm pressure and 25° has a free energy greater than that of 1 mole of carbon dioxide at 1 atm and 25°, and so it is possible for the carbon and oxygen to combine to form carbon diox-

ide at this constant temperature and pressure. However, thermodynamics has nothing to say about the time that will be required, and carbon may exist for a very long time in contact with oxygen; but the reaction is possible and will take place slowly. The reverse process—the decomposition of carbon dioxide—involves an increase in free energy, and it can occur only with the aid of an outside agency or by heating to a very high temperature where the free-energy change has the opposite sign.

TABLE III

Criteria for Equilibrium and Spontaneous Processes

	Spontaneous	Equilibrium	Not Spontaneous
ΔS ($q = 0$)	+	0	−
ΔF (T and p constant)	−	0	+
ΔA (T and v constant)	−	0	+

Early attempts to discover a relation between thermodynamics and the direction of spontaneous chemical reactions led Berthelot in 1879 to the false conclusion that the evolution of heat in a chemical reaction is a measure of chemical affinity. The mere existence of spontaneous reactions which absorb heat and the general reversibility of all reactions under suitable conditions show that this suggestion cannot be right. In some cases, however, where the entropy change is very small, it serves as a rough approximation. This statement follows from the relation, $\Delta F = \Delta H - T\,\Delta S$, at constant temperature and the criterion, $\Delta F < 0$, for spontaneous processes under the conditions usual for carrying out chemical reactions. If $T\,\Delta S$ is small compared with ΔF, as is often true, then ΔH and ΔF will have the same sign and approximately the same magnitude; ΔH will then be negative, and heat will be evolved in the spontaneous reactions with negative values of ΔF.

A qualitative principle known as the theorem of Le Chatelier has been useful in predicting the direction in which a change may be expected. According to this theorem, if a system at equilibrium is disturbed, the system will shift in such a way as to minimize the effect of the disturbance. For example, if pressure is applied to ice, the ice melts to give liquid water, which has a smaller volume, and the pressure is relieved. Other examples are given in later chapters.

Thermodynamic Calculations. The various thermodynamic quantities q, w, H, F, S, E, and A, are understood best through the quan-

titative relations which connect them. In this section simple physical processes are considered. Applications to chemical processes may be found throughout the book. In considering the application of thermodynamic formulas to a given problem, the various restrictions under which these formulas were derived must be borne in mind, and it is well to consider: (*a*) What are the initial and final states? (*b*) Is the process reversible or not? (*c*) Is it isothermal or not? (*d*) Is it isobaric or not; that is, is it carried out at constant pressure?

Example 4. One mole of benzene is vaporized at the boiling point 80.2° or 353.3° K under a pressure of 1 atm. The heat of vaporization measured in a calorimeter at constant pressure is 94.4 cal per gram. Calculate w and q and each of the thermodynamic quantities ΔH, ΔE, ΔA, ΔF, and ΔS. The process is

$$C_6H_6\ (l) \longrightarrow C_6H_6\ (vap)$$

and it is carried out reversibly, isothermally, and at a constant pressure of 1 atm.

$$q_p = \Delta H = 94.4 \times 78.11 = 7374 \text{ cal per mole}$$

Assuming that the volume of the liquid is negligible in comparison with that of the vapor and that the vapor obeys the simple gas laws, we have

$$w = p\,\Delta V = p(V_{\text{vap.}} - V_{\text{liq.}}) \cong^* pV_{\text{vap.}} = RT$$
$$= 1.987 \times 353.3 = 702 \text{ cal per mole}$$
$$\Delta E = \Delta H - p\,\Delta v = 7374 - 702 = 6672$$
$$\Delta A = -w_{\text{max.}} = -p\,\Delta v = -702$$
$$\Delta F = \int v\,dp = 0$$

Also, calculating ΔF in a different way gives

$$\Delta F = \Delta A + p\,\Delta v = -702 + 702 = 0$$

$$\Delta S = \frac{q_{\text{rev.}}}{T} = \frac{7374}{353.3} = 20.87 \text{ entropy units}$$

Also, calculating ΔS in a different way yields

$$\Delta S = \frac{\Delta H - \Delta F}{T} = \frac{7374 - 0}{353.3} = 20.87 \text{ entropy units}$$

Example 5. One mole of an ideal gas at 27.0° changes its pressure from 10 to 1 atm by expanding isothermally and reversibly against a pressure which is gradually reduced. Calculate each of the thermodynamic quantities. Calculations with the simple gas equation show that the volume expands from 2.462 to 24.62 liters.

* The symbol $\cong$ is used to indicate an approximate equality.

The process is carried out isothermally and reversibly, but the pressure is not constant.

$$w_{\max.} = RT \ln \frac{V_2}{V_1} = 1.987 \times 300.1 \times 2.303 \log \frac{24.62}{2.462}$$

$$= 1.987 \times 300.1 \times 2.303 \times 1 = 1373 \text{ cal}$$

$$\Delta A = -w_{\max.} = -1373 \text{ cal}$$

Since the internal energy of an ideal gas is not affected by a change in volume.

$$\Delta E = 0$$

$$q = \Delta E + w = 0 + 1373 = 1373 \text{ cal}$$

$$\Delta H = \Delta E + \Delta(pv) = 0 + 0 = 0$$

since pv is constant for an ideal gas at constant temperature.

$$\Delta F = \int_{10}^{1} v\, dp = RT\,[\ln p]_{10}^{1} = 1.987 \times 300.1 \times 2.303(-1) = -1373 \text{ cal}$$

Also,

$$\Delta F = \Delta A + \Delta(pv) = -1373 + 0 = -1373 \text{ cal}$$

$$\Delta S = \frac{q_{\text{rev.}}}{T} = \frac{1373}{300.1} = 4.58 \text{ entropy units}$$

Also,

$$\Delta S = \frac{\Delta H - \Delta F}{T} = \frac{0 - (-1373)}{300.1} = 4.58 \text{ entropy units}$$

Example 6. One mole of an ideal gas expands isothermally at 27° into an evacuated vessel until the pressure drops from 10 to 1 atm; that is, it expands from a vessel of 2.462 liters into a connecting vessel such that the total volume is 24.62 liters. Calculate the change in thermodynamic quantities.

This process is isothermal, but it is *not* reversible, and the pressure is not constant.

$w = 0$ because the system as a whole is closed and no external work can be done.

$q = 0$ because, according to the Joule–Gay-Lussac effect, there is no heat change in the vessel as a whole during the expansion of an ideal gas.

ΔA and ΔF cannot be calculated directly from w, because the work is not maximum work, and ΔS is not equal to q/T, because the heat is not measured in a reversible process. But these quantities are independent of the path, and their differences between initial and final state are identical with those of the preceding example 5 carried out under conditions which permit their calculation.

Then,

$$\Delta F = -1373 \text{ cal}, \qquad \Delta A = -1373 \text{ cal}, \qquad \Delta H = 0, \qquad \Delta E = 0,$$

$$\Delta S = 4.58 \text{ entropy units}$$

Conversion of Heat into Work. When a system goes through a series of changes which bring it back to its original state (a cyclic process), no work can be produced from heat absorbed if the temperature is maintained constant. However, when heat can be removed at a lower temperature, some heat can be converted into work, and the maximum work obtainable can be calculated as shown in the following derivation. A reversible engine is assumed, for only in a reversible process can the maximum work be obtained.

Consider an engine which performs the following steps reversibly (Carnot cycle): q_2 units of heat are taken in at temperature T_2, the temperature is changed to T_1 by an adiabatic process (such as adiabatic expansion of a gas in the engine), q_1 units of heat are rejected to the surroundings at the lower temperature T_1, and the cycle is then completed by an adiabatic process which raises the temperature to T_2 and restores the system to its original state. The engine gains entropy q_2/T_2 at the higher temperature, loses entropy q_1/T_1 at the lower temperature, and suffers no change in entropy in the adiabatic steps, because in these steps $q = 0$. The entropy change in the engine is zero for a complete cycle because the engine returns to its original condition and therefore to its original entropy. Then,

$$\frac{q_2}{T_2} - \frac{q_1}{T_1} = 0 \tag{37}$$

For the complete cycle ΔE is zero also, and, by the first law, the work done per cycle is given by

$$w = q_2 - q_1 \tag{38}$$

Solving equation 37 for q_1 and substituting in equation 38, we obtain

$$w_{\text{max.}} = q_2 \frac{T_2 - T_1}{T_2} \tag{39}$$

wherein we have explicitly indicated that the work obtained is a maximum, since the process is reversible.

This important equation, which may be regarded as a mathematical statement of the second law of thermodynamics, is independent of the properties of the substance in the engine and of the engine itself, provided it undergoes a Carnot cycle. It shows that the maximum fraction of heat which can be converted into work, that is, $w_{\text{max.}}/q_2$, or the maximum efficiency of the process, is equal to the difference in temperature divided by the higher absolute temperature. If the condenser could be placed at absolute zero all the heat would be available for doing work, and the maximum efficiency would be unity. This equation 39 finds important applications in engineering.

Example 7. What is the maximum work that can be obtained from 1000 cal of heat supplied to a water boiler at 100° if the condenser is at 20°?

$$w_{\text{max.}} = q_2 \frac{T_2 - T_1}{T_2} = (1000) \frac{373.1 - 293.1}{373.1} = 214 \text{ cal}$$

If the boiler temperature is raised to 150° by the use of superheated steam under pressure, how much more work can be obtained?

$$w_{\text{max.}} = (1000) \frac{423.1 - 293.1}{423.1} = 307 \text{ cal}$$

$$307 - 214 = 93 \text{ cal more}$$

Mercury engines have been successfully operated, and their thermodynamic efficiency is higher than that of steam engines because the boiler temperature is 723° K; but the advantage is offset by the initial cost of mercury, the great weight, and the danger from poisoning by mercury vapor.

A relation of the same form as equation 39 was derived by Carnot for an ideal gas put through a Carnot cycle, which in this case consists of an isothermal expansion at T_1, adiabatic expansion to T_2, isothermal compression at T_2, and finally an adiabatic compression to T_1. The details are given in the appendix on page 676. The second law as derived in equation 39 is general, whereas the Carnot cycle is derived only for an ideal gas.

The temperature used in deriving equation 39 was introduced in equations 1 and 2 and called the thermodynamic absolute temperature without further discussion, whereas the temperature used in the derivation in the appendix leading to the same relation is the absolute temperature of ordinary usage, defined in terms of the properties of ideal gases. Hence, both temperature scales are essentially the same, and, if one degree on the thermodynamic scale is taken equal to 1° C, the scales become identical.

The Gibbs–Helmholtz Equation. Another important relation is obtained by differentiating equation 12 with respect to temperature at constant pressure.

$$\left(\frac{\partial F}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_p - S \tag{40}$$

The second and third terms are both equal to c_p. They cancel out, leaving

$$\left(\frac{\partial F}{\partial T}\right)_p = -S \tag{41}$$

In words, the derivative of free energy with respect to temperature at constant pressure is equal to the negative of the entropy.

Substituting the equivalent of $-S$ from equation 12 gives

$$\left(\frac{\partial F}{\partial T}\right)_p = \frac{F - H}{T} \tag{42}$$

or, taking the values of F and H in the initial and final states of an isothermal process,

$$\left(\frac{\partial \Delta F}{\partial T}\right)_p = \frac{\Delta F - \Delta H}{T} \tag{43}$$

According to this equation, the difference between the change in free energy and the change in enthalpy for an isothermal process, divided by the absolute temperature, is equal to the rate at which the difference in free energy changes with temperature, when the pressure is kept constant. This important equation is known as the Gibbs–Helmholtz equation. It is illustrated in detail in a later chapter (page 440).

REFERENCES

Glasstone, "Thermodynamics for Chemists," D. Van Nostrand Co., New York, 1947.

Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

Steiner, "Introduction to Chemical Thermodynamics," McGraw-Hill Book Co., New York, 1941.

MacDougall, "Thermodynamics and Chemistry," John Wiley & Sons, New York, 1939.

Hougen and Watson, "Chemical Process Principles II, Thermodynamics," John Wiley & Sons, New York, 1947.

PROBLEMS

1. A mole of steam is condensed at 100°, and the water is cooled to 0° and frozen to ice. What is the entropy change? Consider that the average specific heat of liquid water is 1.0. Heats of vaporization and fusion are 539.7 and 79.7 per gram.

Ans. $\Delta S = -36.9$ e u.

2. Calculate the molal entropy of liquid chlorine at its melting point, 172.12° K, from the following data obtained by Giauque and Powell:

T °K	15	20	25	30	35	40	50	60
C_p cal degree^{-1} mole^{-1}	0.89	1.85	2.89	3.99	4.97	5.73	6.99	8.00
T °K	70	90	110	130	150	170	172.12	
C_p cal degree^{-1} mole^{-1}	8.68	9.71	10.47	11.29	12.20	13.17	m.p.	

Heat of fusion = 1531 cal per mole.

A plot of C_p/T against T is most convenient for the graphical integration. Below 15° it may be assumed that C_p is proportional to T^3. *Ans.* 24.9 e u.

3. A thermostat was maintained at a temperature of 96.9°. The air in the room was at 26.9°. During a certain length of time 1000 cal of heat leaked through the thermostat insulation into the room.

(*a*) What was the entropy change of the material in the thermostat?

(*b*) What was the entropy change of the air in the room?

(*c*) Was the process reversible or irreversible?

Ans. (*a*) −2.70 e u; (*b*) 3.33 e u;

(*c*) Total entropy change = 0.63 e u, therefore irreversible.

4. Tabulate: (*a*) w, (*b*) q, (*c*) ΔH, (*d*) ΔE, (*e*) ΔF, (*f*) ΔA, (*g*) ΔS when 1 mole of steam is compressed reversibly to liquid water at the boiling point 100°. The heat of vaporization of water at 100° and 760 mm is 539.7 cal per gram.

Ans. (*a*) −743 cal. (*b*) −9720 cal. (*c*) −9720 cal. (*d*) −8977 cal.
(*e*) 0. (*f*) 743 cal. (*g*) −26.0 e u.

5. One liter of a perfect gas at 300° K has an initial pressure of 15 atm and is allowed to expand isothermally to a volume of 10 liters.

(*a*) Calculate the maximum work which can be obtained from the expansion. Calculate (*b*) ΔE, (*c*) ΔH, (*d*) ΔF, (*e*) ΔA.

Ans. (*a*) 830 cal. (*b*) 0. (*c*) 0. (*d*) −830 cal. (*e*) −830 cal.

6. Derive an expression for the difference in entropy of 1 mole of an ideal gas with constant heat capacities at a temperature T_1 and pressure p_1 and at temperature T_2 and pressure p_2 by calculating the entropy changes when 1 mole of the gas is heated from T_1 to T_2 at constant pressure p_1 and then is isothermally and reversibly compressed from p_1 to p_2.

$$\textit{Ans.} \quad \Delta S = C_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1}.$$

7. Theoretically, how high could a gallon of gasoline lift an automobile weighing 3200 lb against the force of gravity, if it is assumed that the cylinder temperature is 2200° and the exit temperature 1200°? (Density of gasoline = 0.8; 1 lb = 453.6 g; 1 ft = 30.48 cm; 1 liter = 0.2642 gal. Heat of combustion of gasoline = 11,200 cal per gram.) *Ans.* 13,200 ft.

---

8. Calculations with the Debye formula show the molal entropy of silver iodide to be 1.5 entropy units at 15° K. From the following data for the molar heat capacity of constant pressure, calculate the molal entropy of silver iodide at 298.1° K:

$T°$	C_p	$T°$	C_p	$T°$	C_p	$T°$	C_p
21.00	3.82	64.44	9.36	145.67	11.92	258.79	13.05
30.53	5.23	88.58	10.60	170.86	12.15	273.23	13.26
42.70	7.09	105.79	11.19	198.89	12.49	287.42	13.48
52.15	8.20	126.53	11.60	228.34	12.76	301.37	13.64

9. One mole of nitrobenzene $C_6H_5NO_2$ is vaporized at 210°. The heat of vaporization at this temperature is 79.1 cal per gram. Calculate (*a*) q, (*b*) w, (*c*) ΔH, (*d*) ΔE, (*e*) ΔF, (*f*) ΔA, (*g*) ΔS.

10. Ten grams of helium is compressed isothermally and reversibly at 226.9° from a pressure of 2 atm to 10 atm. Calculate (*a*) q, (*b*) w, (*c*) ΔF, (*d*) ΔA, (*e*) ΔH, (*f*) ΔE, (*g*) ΔS.

11. Calculate each of the quantities listed in Problem 10 for the isothermal compression of the helium not reversibly, but with a pressure of 10 atm applied directly.

12. One mole of NH_3 (considered to be a perfect gas) initially at 25° and 1 atm pressure is heated at constant pressure until the volume has trebled. Calculate (*a*) q, (*b*) w, (*c*) ΔH, (*d*) ΔE, (*e*) ΔS. For NH_3, $C_p = 6.70 + 0.0063T$.

13. In the reversible isothermal expansion of an ideal gas at 300° K from 1 liter to 10 liters, where the gas has an initial pressure of 20 atm, calculate (*a*) ΔS for the gas, (*b*) ΔS for all systems involved in the expansion, (*c*) ΔA for the gas, (*d*) ΔA for all systems involved in the expansion.

14. Calculate the theoretical maximum efficiency with which heat can be converted into work in the following hypothetical turbines:

(*a*) Steam at 100° with condenser at 40°.

(*b*) Mercury vapor at 360° with condenser at 140°.

(*c*) Steam at 400° and condenser at 150°.

(*d*) Air at 800° and exit at 400°.

(*e*) Air at 1000° and exit at 400°, special alloys being used.

(*f*) Helium at 1500° and exit at 400°, heat from atomic energy being used.

15. Show that the coefficient of performance of a refrigeration machine, defined as the ratio of the heat absorbed by the refrigeration fluid at the low temperature T_2 to the work done by the compressor on the fluid, is $T_2/(T_1 - T_2)$ for reversible operation. The cycle consists of absorption of heat by the fluid in the evaporator at T_2, reversible adiabatic compression which raises the temperature to T_1, rejection of heat in the condenser at T_1, and reversible adiabatic expansion which lowers the temperature to T_2. How much work must be done in a refrigerating machine, operating in a Carnot cycle between 0 and 25°, in order to freeze 100 kg of water?

16. Calculate the change in entropy of a mole of water when it is cooled at 1 atm from vapor at 200° to liquid at 25°. C_p for steam $= 7.00 + 0.00277T$, C_p for water $= 1.0$, and heat of vaporization $= 539.7$ cal per gram.

17. Calculate the differences between the atomic entropies of Hg (*l*) and Hg (*s*) at −50°. The melting point of Hg is −39°, and the heat of fusion is 560 cal per gram-atom. The heat capacity per gram-atom of Hg (*l*) may be taken as $7.1–0.0016T$ and that of Hg (*s*) as 6.4 cal per degree.

18. (*a*) Calculate the external work done against the atmosphere when 1 mole of toluene is vaporized at its boiling point, 111°. The heat of vaporization at this temperature is 86.5 cal per gram.

For the vaporization of 1 mole, calculate (*b*) q, (*c*) ΔH, (*d*) ΔE, (*e*) ΔF, (*f*) ΔA, (*g*) ΔS.

19. Calculate (*a*) w, (*b*) ΔA, and (*c*) ΔF when one mole of liquid water is evaporated at its boiling point 100° at 1 atm and then expanded in its vapor state from 30.5 to 50 liters at 100°.

20. A thermodynamic system goes through a cycle consisting of two steps. In the first step 1000 joules of work is performed by the system on the surroundings, and 500 cal of heat is absorbed by the system. In the second step 700 joules of work is done on the system. How much heat is absorbed by the system in the second step?

21. One mole of an ideal gas in 22.4 liters is expanded isothermally and reversibly at 0° to a volume of 224 liters and $\frac{1}{10}$ atm.

Calculate (*a*) w, (*b*) q, (*c*) ΔH, (*d*) ΔF, (*e*) ΔS for the gas.

One mole of an ideal gas in 22.4 liters is allowed to expand irreversibly into an evacuated vessel such that the final total volume is 224 liters.

Calculate (*f*) w, (*g*) q, (*h*) ΔH, (*i*) ΔF, (*j*) ΔS for the gas.

Calculate (*k*) ΔS for all the systems involved in (*e*) and (*l*) ΔS for all the systems involved in (*j*).

22. Discuss the advantages and disadvantages of using diphenyl instead of water for an engine. Diphenyl boils at 254.6° and melts at 70.5°.

23. An ideal gas expands isothermally and reversibly from a state of p_1 and v_1 to a state of p_2 and v_2. Calculate the work done by the gas and also the $\int v\,dp$ term. What is the change in the product of p and v?

An actual gas which obeys the relation $p(v - b) = RT$, where b is a constant, under certain conditions expands isothermally and reversibly from a state of p_1 and v_1 to a state of p_2 and v_2. Calculate the work done and also the term $\int v\,dp$. What is the change in the product of p and v? What general conclusion can be drawn from these results?

24. A system at a temperature of 300° K, under a constant pressure of 1 atm and occupying a volume of 2 liters, is heated to a temperature of 400° K. During the heating, the system absorbs 10 cal per degree rise in temperature. The system occupies a volume of 3 liters at 400° K. Calculate (*a*) ΔE, (*b*) ΔH, (*c*) ΔS for the system.

25. A 2-liter container at 0° contains H_2S (assumed to be an ideal gas) at 1 atm pressure. The gas is heated to 100°, the external pressure remaining 1 atm. Calculate (*a*) the heat absorbed, (*b*) the work done, (*c*) ΔE, (*d*) ΔH, and (*e*) ΔS. For H_2S, $C_p = 7.15 + 0.00332T$.

---

26. (*a*) Calculate the least work which would have to be performed in order to extract 100 cal of heat from an ice bath at 0°, when the surroundings are at 25°.

(*b*) How much heat at 25° could be obtained from the ice bath on the expenditure of 10 cal of work?

27. For a reversible process the net ΔS for all systems involved is equal to zero. Show that in an *isothermal* process the net ΔA for all systems involved is also equal to zero.

28. An isothermal irreversible process takes place at 300° K so that the net gain in entropy for all systems involved is +10.0 entropy units. Calculate the minimum amount of work which would have to be transformed into heat at 300° K to restore the systems involved to their previous state.

29. One-half mole of an ideal monatomic gas initially at 25° and occupying a volume of 2 liters is allowed to expand adiabatically against a constant pressure of 1 atm until external and internal pressures are equal. The gas is then compressed isothermally and reversibly until its volume is 2 liters at the lower temperature. Calculate (*a*) q, net heat absorbed, (*b*) w, net work done, (*c*) ΔE, (*d*) ΔH, and (*e*) ΔS.

CHAPTER IX

THE LIQUID STATE

Theory of Liquids. A liquid has no definite shape, but it does retain a definite volume under given conditions. The distance between molecules is much less in liquids than in gases, as illustrated by the fact that a mole of liquid water at 100° occupies 18.8 ml, but when vaporized it occupies about 30,200 ml at 1 atm pressure. This closer proximity of molecules in the liquid state and a corresponding restriction of their movements result in a lesser fluidity and make the effect of pressure and temperature much less in the case of a liquid than a gas.

The internal energy in the vapor state is greater than in the liquid state because it is necessary to supply energy in order to overcome the force of attraction which holds the molecules close together in the liquid.

A liquid may be regarded as a condensed gas or as a melted solid, and each point of view is important. The theory of liquids is in a much less satisfactory state than the theories of gases and crystals, but important progress is being made in our understanding of the structure of liquids.*

At any instant liquids do possess something analogous to a definite arrangement between neighboring molecules as shown by the patterns they exhibit when X-rays are passed through them. Moreover they require the expenditure of energy when one layer of liquid is forced past another. These facts and many more seem to be explained best on the hypothesis that the molecules are squeezed together by their own forces of mutual attraction but that each molecule has a free volume surrounding it, in which it behaves effectively as an ideal gas. In a solid the molecules cannot move from one place to another, but in a liquid they can, provided that a small amount of energy is supplied. The thermodynamic properties of a liquid, such as vapor pressure, specific heat, and entropy of fusion, can be expressed in terms of this free volume.

Liquefaction of Gases. More than a century ago, Faraday liquefied practically all the gases which condense at moderate pressures and not too low temperatures. He inverted a sealed-off U tube and heated one end while the other was immersed in a freezing mixture. Thus, when crystals of chlorine hydrate were heated in this tube, the liberated chlo-

* Hirschfelder, The Structure of Liquids, *J. Chem. Education*, **16**, 540 (1939); Frenkel, "The Kinetic Theory of Liquids," Clarendon Press, 1946.

rine gas was put under such a high pressure that it condensed to a yellow liquid in the cold end of the tube.

In 1834 Thilorier liquefied carbon dioxide in rather large amounts and observed that the evaporating liquid became sufficiently cold to freeze. He was able to obtain a temperature of $-100°$ C by placing a mixture of solid carbon dioxide and ether under reduced pressure.

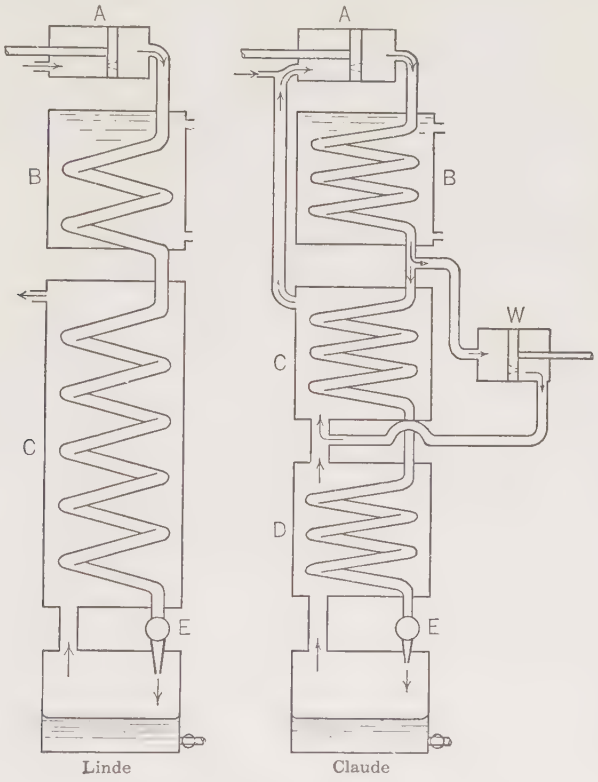


FIG. 41. The liquefaction of gases.

The following principles are involved in the liquefaction of gases: (1) the gas must be below its critical temperature; (2) the pressure must be great enough to cause liquefaction, and the lower the temperature the lower is the required pressure; (3) the incoming gas is cooled by the outgoing gas which has been cooled by expansion; (4) the gas is cooled by doing external work in an engine; and (5) it is cooled by expanding against the force of attraction between the molecules as explained in the discussion of the Joule–Thomson effect.

Air was first liquefied in large quantities in 1895. The operating principle of the Linde process and the Claude process are indicated in **Fig. 41.**

In both processes the gas is compressed in a pump shown at A and passed through a coil in B which is cooled with a refrigerant such as liquid ammonia, and, then, after further cooling in C and D, it is forced through a small opening E where it falls to atmospheric pressure. This large expansion causes a marked cooling, and the cold gas passes up around the gas in the coils and cools them still further. This cooling of the incoming gas by the colder outgoing gas continues until finally the gas leaving the jet E is so cold that the additional cooling from expansion causes a part of it to liquefy and fall to the bottom of the container where it is drawn off and stored in vacuum-jacketed vessels.

The Linde process makes use only of the cooling due to this expansion of air against molecular attraction, and in spite of its extensive use it is inefficient from a theoretical standpoint. In laboratory units it operates at about 200 atm and produces nearly a liter of liquid air per kilowatt-hour.

Instead of allowing the energy of compression to be wasted by free expansion into the atmosphere, as is done in the Linde process, the Claude process conserves some of it by passing a large fraction of the compressed gas through an engine W. The work done by this engine helps to operate the compressor A, and so the total power consumption is reduced. After doing work in the engine W, the gas is colder and serves to cool further the rest of the gas which is passing through the coils in chamber C. Still further cooling preparatory to expansion and liquefaction takes place in chamber D. Although this process is much more efficient than the one in which none of the energy of compression is recovered as useful work, there are practical difficulties in operating an expansion engine at low temperatures, because of the problem of lubrication and unequal thermal expansion of the moving parts.

The liquefaction of gases finds extensive application. Ammonia, sulfur dioxide, methyl chloride, and Freon (CF_2Cl_2) are among the gases used in refrigeration. A gas suitable for refrigeration should have suitable boiling and freezing points, a high critical temperature, and a large heat of vaporization. It should be stable, nonpoisonous, and inexpensive.

Solid carbon dioxide, known as "dry ice," is also much used as a refrigerant and as a substitute for ice. It is lighter than ice. It leaves no water or objectionable residue on being heated, and it can be kept in small containers for several hours. When foods are frozen very rapidly by means of "dry ice," their texture is preserved. A vacuum bottle of dry ice in acetone gives a convenient mixture at about $-80°$ C for laboratory experimentation.

Many gas mixtures can be separated by liquefaction. The fractional

distillation of liquid air is the chief source of commercial nitrogen and oxygen. If the cost of liquefying air could be reduced, many new uses for oxygen would arise, particularly in blast furnaces and combustion operations involving the production of high temperatures. Oil–oxygen furnaces might replace electric furnaces, for example, in the production of calcium carbide. The use of oxygen has expanded already to such an extent that cheap oxygen is now transported in large insulated tank cars and tank trucks.

The production of liquid oxygen at $2.75 per ton has been considered in developing large-scale operations. Small-scale units for liquefying air have been developed recently.*

Through the use of oxygen instead of air it is possible to eliminate nitrogen from combustion processes. In this way coal and organic matter can be converted into carbon monoxide by a continuous process; or with steam into carbon monoxide and hydrogen. These gases are finding extensive use in the production of synthetic gasoline and may eventually lead to a more economical use of coal at the mine.

The rare gases of the atmosphere, neon and argon, used in electric lamps, can be recovered as by-products in the liquefaction of air. Formerly regarded as laboratory curiosities, they now find wide use in electric lighting—neon in high-voltage colored lights and signs, and argon in tungsten-filament lamps.

The removal of moisture from air by passage through tubes in a refrigerating bath, the recovery of helium from natural gas, and the production of liquid propane in tanks for household cooking are among the many industrial applications of the liquefaction of gases. The important laboratory investigations of specific heats at low temperatures are dependent on liquid air, liquid hydrogen, and liquid helium.

Vapor Pressure of Liquids. According to the kinetic theory there is a continuous flight of molecules from the surface of a liquid into the free space above it. At the same time molecules of gas or vapor † return to the surface of the liquid at a rate depending on the concentration of the vapor. Eventually, a condition of equilibrium is established between the liquid and its vapor, when the rate of escape is exactly equal to the rate of condensation of vapor. The vapor is then said to be *saturated*. The pressure exerted by vapor which is in equilibrium with the liquid is known as the *vapor pressure*. The equilibrium between a liquid and its vapor is dependent on the temperature. For every temperature below

* Keyes, *Chem. Rev.*, **39,** 449 (1946).

† A vapor is generally defined as an easily liquefiable gas as distinguished from permanent gases such as nitrogen and hydrogen which must be cooled far below room temperature before becoming liquid at atmospheric pressure.

the critical temperature, there is a certain pressure at which vapor and liquid may exist in equilibrium in all proportions; and, conversely, for every pressure below the critical pressure, there is a certain temperature at which vapor and liquid may exist in equilibrium in all proportions. In the special case where the pressure is 760 mm, this temperature is the standard boiling point of the liquid. The vapor pressure of a liquid is a constant quantity at any temperature and is independent of the amounts of liquid and vapor present, but it increases as the temperature is raised. Table I gives the vapor pressure of several typical liquids from 0 to 100°. These data are plotted in **Fig. 42** on rectangular coordinates, and in **Fig. 43** the logarithms of the vapor pressure in millimeters are plotted against the reciprocals of the absolute temperature. The reciprocals of

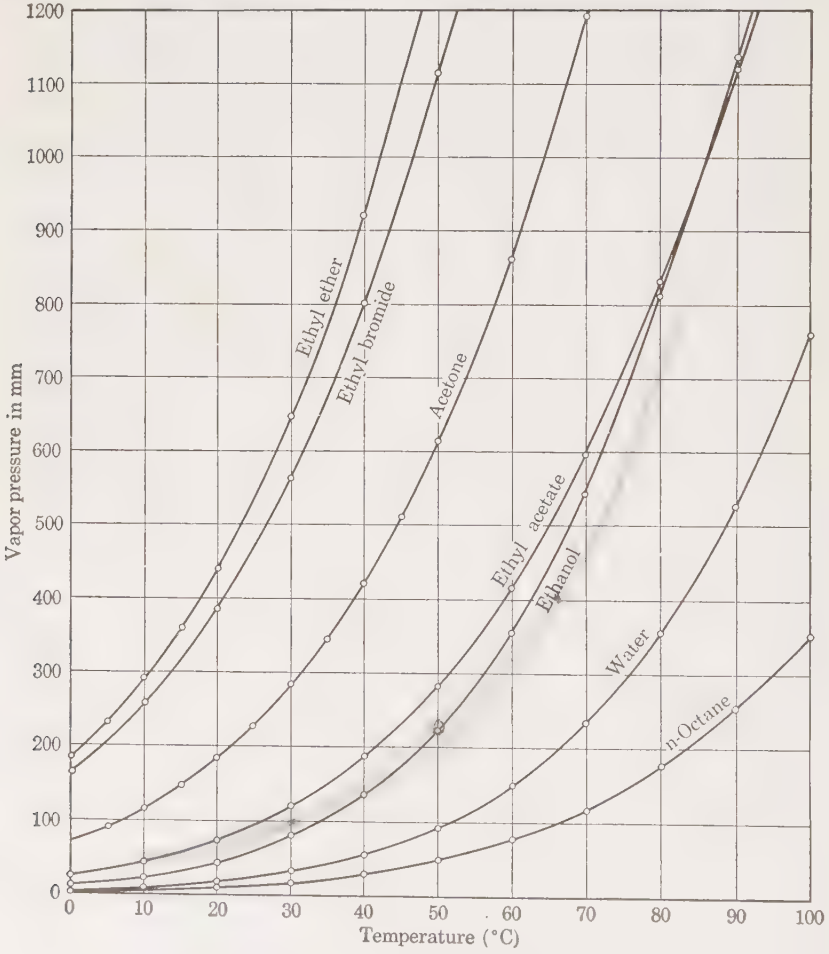


FIG. 42. Vapor-pressure–temperature curves for seven common liquids.

TABLE I

VAPOR PRESSURES OF LIQUIDS IN MILLIMETERS OF MERCURY

$t°$ C	Water	Ethyl Ether	Ethyl Bromide	Acetone	Ethyl Acetate	Ethanol	n-Octane
0	4.58	185.3	165		24.2	12.2	2.9
10	9.21	291.7	257	115.6	42.8	23.6	5.6
20	17.54	442.2	386	184.8	72.8	43.9	10.4
30	31.82	647.3	564	282.7	118.7	78.8	18.4
40	55.32	921.3	802	421.5	186.3	135.3	30.8
50	92.51	1277.0	1113	612.6	282.3	222.2	49.3
60	149.38		1512	866.0	415.3	352.7	77.5
70	233.7			1200.0	596.3	542.5	117.9
80	355.1				832.8	812.6	174.8
90	525.76				1133.0	1187.0	253.4
100	760.0				1520.0		353.6

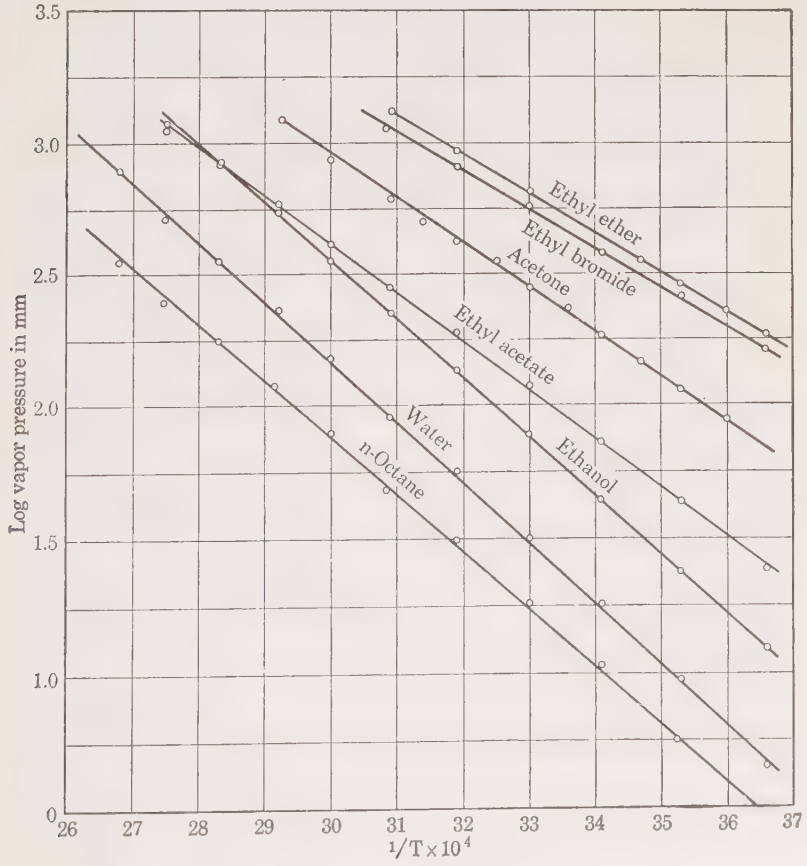


FIG. 43. Log p vs $1/T$ curves for the liquids shown in Table I.

the absolute temperature have been multiplied by 10^4 for convenience in plotting. Thus, 0° or 273.1° K gives for $1/T$ a value of 0.00366 or 36.6×10^{-4} as shown at the extreme right.

These graphs follow as a first approximation the equation,

$$\log p = \frac{A}{T} + B \tag{1}$$

where p is the vapor pressure and A and B are constants.

Example 1. Draw the best straight line through the points obtained by plotting log vapor pressure of iodobenzene against the reciprocal of the absolute temperature. At 70° the vapor pressure is 13.65 mm, at 110° it is 73.88, and at 170° it is 479.7 mm.

(*a*) Find the equation for this straight line.

$$\log p = \frac{A}{T} + B$$

$$A = \text{slope} = -2.370 \times 10^3$$

$$B = y \text{ intercept} = 8.041$$

$$\log p = \frac{-2370}{T} + 8.041$$

(*b*) Calculate the vapor pressure at 0°.

$$\log p = \frac{-2370}{273.1} + 8.041 = -0.637; \qquad p = 0.231 \text{ mm}$$

(*c*) Calculate the boiling point, that is, the temperature at which the pressure is 760 mm.

$$\log 760 = \frac{-2370}{T} + 8.041$$

$$T = \frac{2370}{8.041 - \log 760} = 459.3° \text{ K} = 186.2° \text{ C}$$

Measurement of Vapor Pressure. The boiling temperatures of a liquid may be determined at various pressures using a vacuum or pressure pump to change the pressure and a manometer to measure it. The thermometer is not immersed in the liquid, because the liquid may become superheated. It is supported so that the vapor condenses on it and

bathes the thermometer bulb with liquid, which is in equilibrium with the vapor at the measured pressure. In another method the liquid is allowed to drip slowly over the thermometer bulb while it is heated by the condensation of vapor. There is no danger of superheating the liquid above its normal boiling temperature if the heat is supplied only by the condensing vapor. Care must be taken to insure that all dissolved air or other gas is boiled out before the measurements are taken; otherwise the total pressure as measured by the manometer will be larger than the true pressure of the pure vapor.

The *gas-saturation method* is an accurate and convenient method for determining the vapor pressure of a liquid. A current of pure dry air or other gas is bubbled slowly through a weighed amount of the liquid whose vapor pressure is to be determined. The liquid is maintained at constant temperature, and its loss in weight is measured. The vapor may be removed from the gas stream in an absorption tube and weighed, or the liquid in the vessel may be weighed before and after. In passing through the saturating vessel the air absorbs an amount of vapor directly proportional to the vapor pressure of the liquid. The accuracy of this method depends, of course, on having the gas completely saturated with vapor, and, in order to give ample contact with the liquid, the gas is often passed through two or more vessels of liquid in series.

If v is the volume which contains g grams of the vaporized liquid having the molecular weight M, and p is the pressure of the vapor in equilibrium with the liquid at the temperature T, then the vapor pressure p of the liquid is calculated from the ideal-gas laws by the formula,

$$pv = \frac{g}{M} RT$$

or

$$p = \frac{g}{Mv} RT \tag{2}$$

For approximate calculations the volume v occupied by the vapor may be taken as the volume of the dry air measured before it becomes saturated with the vapor. For more accurate calculation or for high vapor pressures, allowance must be made for the fact that the total volume of the gases is increased by the introduction of the vapor. The volume v, of both air and vapor through which the vapor molecules are distributed, is $v' \frac{P}{P - p}$ where v' is the volume of the pure air before

saturation, P is the barometric pressure, and p is the vapor pressure of the liquid. Then,

$$p = \frac{g}{M}\frac{RT}{v} = \frac{g}{M}\frac{RT}{\frac{v'P}{P-p}}$$

$$p\left(1 + \frac{g}{M}\frac{RT}{v'P}\right) = \frac{g}{M}\frac{RT}{v'}$$

$$p = \frac{\frac{gRT}{Mv'}}{1 + \frac{gRT}{Mv'P}} \tag{3}$$

Example 2. When liquid bromobenzene was vaporized at 30.0° by passing 20.00 liters of dry air through it, the loss in weight of the liquid was 0.9414 g. The barometric pressure was 760 mm. The molecular weight is 157.0. Approximately, what is the vapor pressure at this temperature?

$$p = \frac{g}{M}\frac{RT}{v} = \frac{0.9414 \times 0.08205 \times 303.1}{157.0 \times 20.00} = 0.00746 \text{ atm}$$

$$p = 0.00746 \times 760 = 5.67 \text{ mm}$$

More exactly, what is the vapor pressure, if equation 3 is used?

$$p = \frac{0.00746}{1 + \frac{0.00746}{1}} = 0.00740 \text{ atm}$$

$$p = 0.00740 \times 760 = 5.62 \text{ mm}$$

The difference between the use of equation 2 and equation 3 is much more pronounced with materials of high vapor pressure.

The Clapeyron Equation. The theoretical explanation of the empirical relation between vapor pressure and temperature was developed by Clapeyron in 1834. Consider a liquid in equilibrium with its vapor at a temperature T and a pressure equal to the vapor pressure p at that temperature. If some of the liquid is vaporized at this equilibrium pressure and temperature, by equation 36 of Chapter VIII,

$$\Delta F = 0$$

Since the free energy of the whole system does not change in this case, the decrease in free energy of the liquid phase due to the loss of a given weight of liquid, 1 g, for example, must equal the increase in free energy of the vapor phase due to the gain of 1 g of vapor.

Representing the free energy of 1 g of the liquid by F_1, and that of 1 g of the vapor by F_2 under these conditions, we may write for the previous equation,

$$F_1 = F_2 \tag{4}$$

If the temperature is raised to $T + dT$, the pressure must be increased to $p + dp$, the vapor pressure at this higher temperature, in order for the two phases to be in equilibrium. Under these conditions the free energy of 1 g of the liquid and of 1 g of the vapor will be $F_1 + dF_1$ and $F_2 + dF_2$, respectively, and, since the change in free energy of the system must be zero for vaporization of the liquid at this equilibrium pressure and temperature,

$$F_1 + dF_1 = F_2 + dF_2$$

Therefore, subtracting equation 4 gives

$$dF_1 = dF_2 \tag{5}$$

By differentiating equation 31 of Chapter VIII,

$$F_1 = E_1 + p_1 v_1 - T_1 S_1$$

we obtain

$$dF_1 = dE_1 + p_1\,dv_1 + v_1\,dp_1 - T_1\,dS_1 - S_1\,dT_1 \tag{6}$$

For a reversible process,

$$dq = T\,dS$$

and by the first law of thermodynamics,

$$dE_1 = dq - dw = T_1\,dS_1 - p_1\,dv_1$$

Substituting for dE_1 in equation 6, we have

$$dF_1 = v_1\,dp_1 - S_1\,dT_1 \tag{7}$$

This relation gives the increase in free energy of 1 g of the liquid when the pressure is increased by dp_1 and the temperature by dT_1; v_1 is the volume and S_1 the entropy of the given weight of liquid at pressure p_1 and temperature T_1. A similar equation holds for the vapor:

$$dF_2 = v_2\,dp_2 - S_2\,dT_2 \tag{8}$$

The subscripts on dp and dT may be dropped in equations 7 and 8 since the temperature and pressure of the two phases are the same. Setting these two equations equal as justified by equation 5 gives

$$v_1\,dp - S_1\,dT = v_2\,dp - S_2\,dT$$

or, on rearranging,

$$\frac{dp}{dT} = \frac{S_2 - S_1}{v_2 - v_1} \tag{9}$$

Also, we have

$$S_2 - S_1 = \frac{l}{T} \tag{10}$$

where l is the heat of vaporization of a gram of the liquid at this temperature and pressure. Substituting from equation 10 into equation 9, we obtain the Clapeyron equation:

$$\frac{dp}{dT} = \frac{l}{T(v_2 - v_1)} \tag{11}$$

This equation gives the rate of change of the vapor pressure of a liquid with temperature, dp/dT, in terms of the heat of vaporization l, volume v_1 of the liquid, and volume v_2 of the vapor at the temperature T and pressure p. The quantities l, v_1, and v_2 all apply to the same weight of material.

In using this equation it is necessary to have the units consistent; that is, the heat term must be expressed in the same units as the product of pressure and volume change. If the pressure is given in atmospheres and volume in liters, the heat may be expressed in liter-atmospheres (1 cal = 0.04129 l-atm); or the pressure may be converted into dynes when the heat is expressed in ergs.

Example 3. What is the rate of change of the vapor pressure of water at 100°? The heat of vaporization is 539.7 cal per gram, the specific volume, that is, the volume occupied by 1 g of liquid water is 1.043 ml, and the specific volume of steam is 1677 ml, all at 100° C and 1 atm. (cal $\times$ 0.04129 = liter-atm.)

$$\frac{dp}{dT} = \frac{539.7 \times 0.04129}{373.1(1.677 - 0.00104)} = 0.0356 \text{ atm per degree}$$

$$760 \times 0.0356 = 27.1 \text{ mm per degree}$$

A formula of the same form as equation 11 may be obtained for the equilibrium between a solid and its vapor or between a pure solid and pure liquid. In the latter case dp/dT gives the change in pressure necessary to change the melting point by dT; l represents the heat of fusion per gram; v_2 is the volume of a gram of the liquid; and v_1 is the volume of the same weight of solid.

Example 4. Calculate the change in the freezing point of water produced by an increase in pressure of 1 atm. At 0° the heat of fusion of ice per gram is 79.7 cal or 3.291 l-atm, the density of water is 0.9998 g per milliliter, and the density of ice is 0.9168. The reciprocals of the densities, 1.0002 and 1.0908, are

the volumes in ml of 1 g. They are divided by 1000 to give liters. For small changes in temperature we may replace dp/dT by $\Delta p/\Delta T$. Then,

$$\frac{\Delta p}{\Delta T} = \frac{3.291}{273.1\left(\frac{1.0002}{1000} - \frac{1.0908}{1000}\right)} = -133 \text{ atm per degree}$$

In words, 133 atm is the pressure required to lower the freezing point of water 1°; and the reciprocal,

$$\frac{\Delta T}{\Delta p} = \frac{-1}{133} = -0.0075° \text{ per atmosphere}$$

shows that an increase in pressure of 1 atm lowers the freezing point 0.0075°. The negative sign indicates that an increase of pressure causes a decrease in temperature, a relation which follows by Le Chatelier's theorem from the fact that the specific volume of ice is greater than that of water at the freezing point.

The Clausius–Clapeyron Equation. Clausius showed how the Clapeyron equation may be simplified by assuming that the vapor obeys the ideal gas law. If 1 mole is taken instead of 1 g, V_2 is the volume of 1 mole of vapor, V_1 is the volume of 1 mole in the liquid state, and $\Delta H_{\text{vap.}}$ is the molar heat of vaporization (molecular weight $\times$ l). Furthermore, V_1 may be considered negligible in comparison with V_2; for example, V_1 for water at 100° is 18.8 ml, and V_2 is 30,200 ml. For V_2 may be substituted its equivalent RT/p. Then,

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap.}}}{T(V_2 - V_1)} = \frac{p\Delta H_{\text{vap.}}}{RT^2}$$

On rearrangement this becomes,

$$\frac{1}{dT}\frac{dp}{p} = \frac{\Delta H_{\text{vap.}}}{RT^2} \tag{12}$$

or,

$$\frac{d \ln p}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2} \tag{13}$$

Since R is a constant, integrating on the assumption that $\Delta H_{\text{vap.}}$ is a constant yields

$$\int d \ln p = \int \frac{\Delta H_{\text{vap.}}}{R} T^{-2}\, dT$$

$$\ln p = -\frac{\Delta H_{\text{vap.}}}{R}\frac{1}{T} + C \tag{14}$$

where C is the integration constant. This is the equation of a straight line, and, when $\ln p$ is plotted against $1/T$, a straight line results, the

slope of which is numerically equal to $-\Delta H_{\text{vap.}}/R$. When logarithms to the base 10 are plotted, the slope is $-\Delta H_{\text{vap.}}/2.303R$. The theoretical justification for the empirical relation given in equation 1 is now apparent.

The slope of the line can be used for calculating the heat of vaporization, thus:

$$\Delta H_{\text{vap.}} \text{ (in calories)} = -(\text{slope of line} \times 2.303 \times 1.987) \qquad (15)$$

Frequently, it is more convenient to use a formula obtained by integrating between limits, p_2 at T_2 and p_1 at T_1, as follows:

$$\int_{p_1}^{p_2} d \ln p = \int_{T_1}^{T_2} \frac{\Delta H_{\text{vap.}}}{R} T^{-2}\, dT$$

$$\ln p_2 - \ln p_1 = \frac{\Delta H_{\text{vap.}}}{R}\left[-\frac{1}{T_2} - \left(-\frac{1}{T_1}\right)\right]$$

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{\text{vap.}}(T_2 - T_1)}{2.303 \times 1.987 \times T_2 \times T_1} \qquad (16)$$

Using this equation it is possible to calculate the heat of vaporization from the vapor pressures at two different temperatures; and, if the heat of vaporization and the vapor pressure at one temperature are known, the vapor pressure at any other temperature may be calculated. Any units of pressure may be taken as long as they are the same units for both pressures, and any units of heat may be used as long as $\Delta H_{\text{vap.}}$ and R are taken in the same units.

The unintegrated expression is most convenient in correcting boiling points for barometric fluctuations. For *small* changes in pressure the change in boiling point with pressure is given approximately by the formula

$$\frac{\Delta T}{\Delta p} = \frac{RT^2}{\Delta H_{\text{vap.}} p} \qquad (17)$$

Since this formula for calculating the heat of vaporization was derived on the assumption that the vapor behaved as an ideal gas, the results obtained by its use are no more accurate than the calculations involving the formula, $pv = nRT$.

Another approximation is involved in the assumption of the constancy of the heat of vaporization. If the data are sufficiently exact and the temperature range sufficiently great, it will be seen that the lines are not exactly straight. The lines would be straight if the heat capacities of the vapor and liquid were both the same and the vapor an

ideal gas. Under such conditions the heat of vaporization and the slope of the line would be constant. When the line is curved, it is possible to determine the heat of vaporization at any temperature by drawing a tangent to the curve at that temperature. In general, the slope of the log p versus $1/T$ line becomes steeper, that is, the heat of vaporization becomes greater at the lower temperatures where more energy is required to pull the molecules apart and put them into the gas phase.

A more exact equation may be obtained by the addition of another term, thus:

$$\log p = \frac{A}{T} + B \log T + \text{constant} \tag{18}$$

The vapor pressure of a large number of substances can be represented by this formula, even up to the critical temperature, with only small errors. The evaluation of the three constants from data at three temperatures by solving simultaneous equations requires accurate computations.

Example 5. If it is assumed that vapor follows the ideal gas law, show that equation 18 can be derived from thermodynamics, and state the physical significance of the constant B.

$$\Delta H_{\text{vap.}} = \Delta H^0_{\text{vap.}} + \int (C_{\text{vap.}} - C_{\text{liq.}})\, dT = \Delta H^0_{\text{vap.}} + \Delta C_p \int dT$$

$$= \Delta H^0_{\text{vap.}} + \Delta C_p T$$

where $\Delta H_{\text{vap.}}$ is the molar heat of vaporization at temperature T, and C_p is the heat capacity at constant pressure, which is independent of temperature. The constant $\Delta H^0_{\text{vap.}}$ is a hypothetical heat of vaporization at absolute zero.

Substituting into equation 13 yields

$$\frac{d \ln p}{dT} = \frac{\Delta H_{\text{vap.}}}{RT^2} = \frac{\Delta H^0_{\text{vap.}} + (\Delta C_p)T}{RT^2} = \frac{\Delta H^0_{\text{vap.}}}{RT^2} + \frac{\Delta C_p}{RT}$$

$$\log p = \frac{-\Delta H^0_{\text{vap.}}}{2.303RT} + \frac{\Delta C_p}{R} \log T + \text{constant}$$

The constant B in equation 18 then is equal to the difference between the heat capacity of the vapor and liquid at constant pressure, divided by the gas constant. This conclusion is only an approximation because the deviations from the ideal gas laws still introduce an appreciable error which is not corrected in this derivation.

There are several useful relations of semiempirical character which give the vapor pressures of liquids at different temperatures. It may be noted that in Fig. 43 the lines seem to be getting closer together at the higher temperatures, that is, at the smaller values of $1/T$. An ideal-

ized graph is shown in **Fig. 44** where all the liquids tend to come to a point at infinite temperature, although, of course, the critical temperatures would be reached long before, and so this hypothetical point has no practical importance. At infinite temperature there would be no intermolecular forces, and all the liquids would tend to behave alike, and all gases would approach the ideal behavior. The different liquids have different heats of vaporization and somewhat different slopes, but the lines are all of the same general character. If one draws horizontal lines at two definite vapor pressures p' and p which are not too far apart, there is a rough proportionality in the temperatures, as one would expect when two parallel lines intersect a series of lines whose slopes are of the same order of magnitude. Thus, the vapor pressure log p is reached by liquid A at temperature T_A and by liquid B at T_B; log p' is reached by liquid A at T_A' and by liquid B at T_B'. Then,

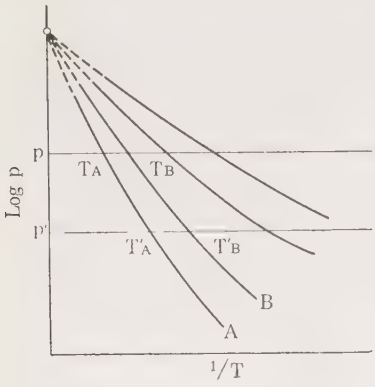


FIG. 44. Hypothetical graph of vapor-pressure curves extrapolated to "infinite temperature" on a log p vs $(1/T)$ plot.

$$\frac{T_B}{T_B'} \cong \frac{T_A}{T_A'}$$

or

$$T_B \cong \frac{T_B'}{T_A'} T_A$$

This relation is known as Duhring's rule, and it is useful for estimating approximately the vapor pressures at various temperatures for any liquid B if the vapor-pressure–temperature data are available for a reference liquid A.

Example 6. Benzene boils at 80° and *n*-hexane at 69°. Benzene has a vapor pressure of 74.7 mm at 20°. At what temperature does *n*-hexane have a vapor pressure of 74.7 mm?

$$T_{n\text{-hexane, 74.7 mm}} = \tfrac{342}{353} \times 293 = 284^\circ \text{K} = 11^\circ \text{C}$$

The experimentally determined temperature is 10° (Table I).

The same principle can be applied in estimating solubilities and several other physical-chemical properties which show a straight-line relationship when the logarithm of the property is plotted against the reciprocal of the absolute temperature.

Graphical methods making use of Duhring's rule are available. The vapor-pressure curve of one reference liquid must be known. Rather exact vapor-pressure relations which are useful for industrial work particularly in the distillation of petroleum, have been reviewed and developed by Watson.*

A practical nomograph is available † for correcting boiling points for pressure with an accuracy of 0.25° or 2 mm pressure. A straightedge is laid across two scales and across a point which is located for each liquid. These points, dependent in a theoretical way on the heats of vaporization, are located for nearly 200 organic liquids, and new points for other liquids can be located when vapor-pressure data are available. There are other empirical rules for converting boiling points of a liquid to the standard boiling points at atmospheric pressure. They depend on the Clapeyron equation and on an empirical rule for the heat of vaporization which is discussed in the following section.

Empirical Vapor Relationships. At higher temperatures the density of the liquid becomes less, but the density of the saturated vapor in equilibrium with the liquid becomes greater. The higher vapor pressure is responsible for the increased vapor density. The two densities approach each other and become equal at the critical temperature. The mean of the densities of any substance in the liquid and vapor states, when plotted against the corresponding temperature, lies on a straight line. The behavior is indicated by the graph shown in **Fig. 45.**‡ This relation, pointed out first by Cailletet and Mathias, is expressed mathematically in equation 19,

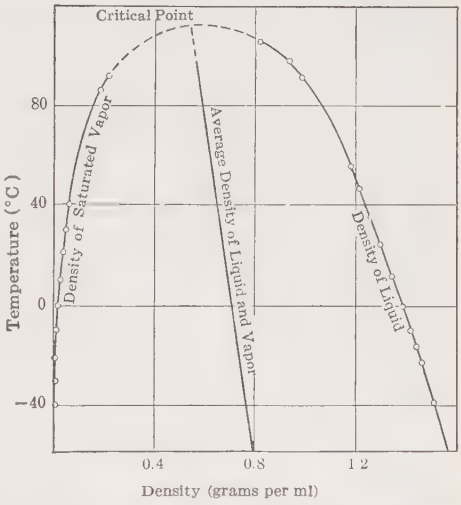


FIG. 45. Densities of liquid and saturated vapor of CCl_2F_2 showing equality of the two at the critical temperature.

$$\frac{d_l + d_v}{2} = AT + B \tag{19}$$

* Watson, *Ind. Eng. Chem.*, **23,** 360 (1931).

† Germann and Knight, *Ind. Eng. Chem.*, **26,** 467 (1934).

‡ From measurements of Bichowsky and Gilkey on CCl_2F_2, *Ind. Eng. Chem.*, **23,** 365 (1931).

where d_l and d_v are the densities of the liquid and saturated vapor, respectively, and A and B are constants. The relation is useful in determining the value of the density of the liquid at the critical temperature, a quantity which frequently cannot be measured directly. The critical volume calculated in this way can be used in evaluating some of the constants in equations of state for gases.

A rough relationship was given in Table II of Chapter II, where it was seen that the standard boiling point (that is, the temperature at which the vapor pressure becomes equal to 1 atm) is equal in many cases to about 0.6 or two thirds of the critical temperature both expressed in absolute temperatures. In this way a very approximate estimate of the critical temperature can be obtained from the boiling point of a given liquid.

Another empirical rule for liquids enables one to estimate the heat of vaporization of a liquid from the temperature at which the liquid boils. According to Trouton's approximate relation, if T denotes the standard boiling point, and $\Delta H_{\text{vap.}}$ the heat of vaporization of 1 mole of liquid, then,

$$\frac{\Delta H_{\text{vap.}}}{T} = 21 \tag{20}$$

In words, the ratio of the molar heat of vaporization to the absolute boiling temperature of a liquid is constant, approximately 21. The relation is shown over a wide range of temperature in Table II.

TABLE II

HEATS OF VAPORIZATION

	Boiling Temp., °C	cal/ gram	$\frac{\Delta H_{\text{vap.}}}{T}$		Boiling Temp., °C	cal/ gram	$\frac{\Delta H_{\text{vap.}}}{T}$
CH_4	−161.4	138.2	19.8	H_2O	100.0	539.7	26.1
HCl	−85.0	98.7	19.2	H_2S	−59.6	132	21.1
$(C_2H_5)_2O$	34.6	83.9	20.2	NH_3	−33.4	327	23.4
$CHCl_3$	61.5	59.0	21.0	HF	17	361	24.9
CCl_4	76.7	46.5	20.4	CH_3OH	64.7	263	24.9
C_6H_6	80.2	94.4	20.8	C_2H_5OH	78.5	204	26.6
$SnCl_4$	112	30.4	20.5	He	−268.9	6	5.7
$C_{10}H_{22}$	160	60.2	19.8	H_2	−252.7	108	10.6
$C_6H_5NO_2$	210	79.1	20.1	CH_3COOH	118.1	96.8	14.8
$C_{10}H_8$	218	75.5	19.7	SO_2	−10.8	94.9	23.1

Trouton's empirical rule has some theoretical significance. The molar heat of vaporization divided by the absolute temperature gives the increase in entropy when a liquid is converted into a vapor. The

change from liquid to vapor leads to increasing disorder, that is, to more random motion of the molecules. The change of entropy is very small at the critical temperature because the liquid and gas are indistinguishable. Accordingly, all liquids would have the same molar entropies of vaporization if measured at their critical temperatures. But it has been pointed out (page 18) that most liquids behave alike not only at their critical temperatures but at equal fractions of their critical temperatures, and we have just seen that the standard boiling points of liquids are in many cases roughly equal fractions of the critical temperatures. Hence, different liquids should have about the same entropy of vaporization at their boiling points, provided that the molecules in liquid and vapor are the same and that no change is involved other than vaporization of the molecules.

When, in addition to the normal force of attraction causing the vaporized material to liquefy, there are other forces which hold molecules tightly together in the liquid state, the heat of vaporization becomes abnormally large. Water, alcohols, ammonia, and other substances with large dipole moments (page 90) require an extra amount of energy for separation of the molecules into the gas phase. Hydrogen and helium, which boil only a little above absolute zero, might well be expected to show large departures from this rule. Acetic acid and carboxylic acids, in general, are abnormal in that the vapor consists of double molecules. An examination of Table II shows that these substances do show marked deviations from the behavior predicted on the basis of Trouton's rule.

The extra attraction which exists between molecules with large dipole moments leads to abnormal behavior not only with respect to Trouton's rule but also with respect to other physical chemical relationships which correlate the behavior of normal liquids—relationships involving such phenomena as surface tension, viscosity, heat capacity, vapor pressures, and behavior on mixing with other liquids.

For "normal" liquids, the molecules of which do not have particularly large dipole moments, example 7 gives an indication of the approximation which may be expected.

Example 7. The boiling point of *n*-heptane is 98°. Estimate roughly (*a*) the heat of vaporization per gram and (*b*) the critical temperature. M = molecular weight.

$$(a)\quad \frac{\Delta H_{\text{vap.}}}{M} = \frac{21T}{M} = \frac{21 \times (273 + 98)}{100} = 77.9$$

$$(b)\quad T_c = \frac{3}{2} T_b = \frac{3 \times 371}{2} = 557 \qquad t_c = 284°$$

The experimentally determined heat of vaporization is 76.4 cal per gram, and the critical temperature is 266°.

Surface Tension. The surface of a liquid possesses special properties which are due to the unbalanced force of molecular attraction at the surface. The molecules at the surface are pulled inward by the other molecules of the liquid, and the liquid tends to adjust itself to give the minimum surface area. This fact explains many common phenomena, including the spherical shape of raindrops, the rise of water in a capillary tube, and the movement of water in blotting paper or in the soil. The surface tension of a liquid, γ, is the force per centimeter on the surface of a liquid which opposes the expansion of the surface area. This definition is illustrated in **Fig. 46** where the force f is pulling on a movable bar against a liquid film which is stretched like a soap-bubble film on a wire frame. Then,

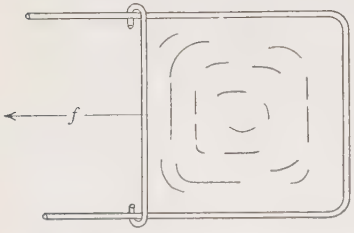


FIG. 46. Illustration of the surface tension of a liquid.

$$\gamma = \frac{f}{2l} \tag{21}$$

where l is the length of the bar in centimeters, and the factor 2 is introduced because there are two liquid surfaces, one at the front and one at the back.

Some liquids, like water, wet the walls of a glass capillary tube, whereas others, like mercury, do not. When a liquid wets the tube, the liquid adhering to the walls pulls the body of the liquid up, but when the liquid does not adhere, the liquid is depressed. In the first instance the surface of the liquid in the tube, called the meniscus, is concave to the horizontal plane. In the second it is convex.

The most accurate method for determining the surface tension of a liquid consists in measuring the height to which it rises in a capillary tube.

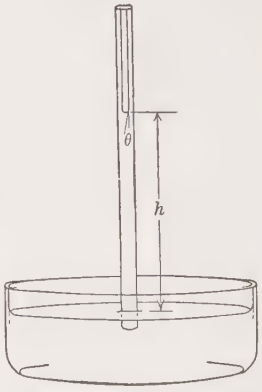


FIG. 47. Rise of a liquid in a capillary tube.

A capillary tube of radius r, as shown in **Fig. 47,** is immersed in a vessel of liquid whose density is d. The liquid wets the tube, and the liquid rises. It continues to rise until the surface tension tending to pull the liquid upward is counterbalanced by the force of gravity pulling it downward. The height to which the meniscus rises at this equilibrium point is denoted by h. The meniscus is curved, and

the average height of the column of liquid is the significant quantity. In ordinary work the height to the bottom of the meniscus is taken, but it would be more exact to add to this height a factor equal to one third of the radius. Then the downward force $= \pi r^2 hdg$ where g is the acceleration of gravity.

The surface makes an angle θ with the walls, and only the vertical component of this force is effective in pulling the liquid upward in the capillary. It acts along the whole length of the surface. Thus, the upward force is,

$$2\pi r\gamma \cos\theta$$

Under stationary conditions at height h the upward and downward forces are equal, and

$$2\pi r\gamma \cos\theta = \pi r^2 hdg$$

or

$$\gamma = \frac{hdgr}{2\cos\theta} \tag{22}$$

For many liquids including water, the angle of contact is very small, θ is nearly 0 and $\cos\theta$ is practically 1. Then,

$$\gamma = \tfrac{1}{2}hdgr \tag{23}$$

Surface tension is expressed in dynes per centimeter.

Surface tension can be measured quantitatively by various other means, including the pulling of a wire ring from the surface of a liquid, the weighing of drops which fall from a special glass tip, the determination of the shape of a hanging drop, the reflection of light from ripples on the surface of a liquid, and the pressure required to blow gas bubbles in the liquid. When the liquid is in contact not with air or its own vapor but with an immiscible liquid, the interfacial tension may be quite different. This property is important in colloid chemistry.

The surface tension of a liquid decreases as the temperature rises, and the molecular agitation increases. At the critical temperature when the liquid becomes indistinguishable from a gas, the surface tension should become practically zero.

In attempting to obtain a quantitative relationship between surface tension and temperature, it is useful to consider the term $\gamma(M/d)^{2/3}$, or $\gamma(Mv)^{2/3}$, where M is the molecular weight in the gaseous state, d the density, and v the volume of 1 g. Then $(Mv)^{2/3}$ is proportional to the surface area of a sphere of liquid containing 1 mole.

Ramsay and Shields found that, for many liquids,

$$\gamma(Mv)^{2/3} = k(t_c - 6 - t) \tag{24}$$

where t is the temperature of the experiment, t_c is the critical temperature of the liquid, and 6 is an empirical constant which tends to make the data fit a better straight line.

The constant k in equation 24 is found to have a value of 2.1 for many liquids.

Example 8. Consider the dimensions of γ and $\gamma(Mv)^{2/3}$.

$$\gamma = \tfrac{1}{2}hdgr = \text{cm}^1(\text{gram-cm}^{-3})(\text{cm-sec}^{-2})\text{cm}^1 = \text{gram sec}^{-2} = \text{dyne-cm}^{-1}$$

$$\gamma\,(Mv)^{2/3} = (\text{dyne-cm}^{-1})\,(\text{cm}^3)^{2/3}\,\text{mole}^{2/3} = \text{dyne-cm mole}^{2/3}$$

This value holds for a large number of nonpolar liquids, such as carbon tetrachloride, benzene, and many organic substances. For certain other liquids such as water or the alcohols or acetic acid, and polar liquids in general, k is found to have values considerably less than 2.1. The same liquids which have abnormal surface-tension behavior possess heats of vaporization larger than are calculated by Trouton's law. The surface tensions of a few common liquids, measured in air, at different temperatures are shown in Table III.

TABLE III

Surface Tension of Liquids in Dynes per Centimeter

Temp., °C	H_2O	CCl_4	C_6H_6	$C_6H_5NO_2$	C_2H_5OH	CH_3COOH
0	75.6	29.0	31.6	46.4	24.0	29.5
25	71.8	26.1	28.2	43.2	21.8	27.1
50	67.9	23.1	25.0	40.2	19.8	24.6
75	63.5	20.2	21.9	37.3	....	22.0

Viscosity. Viscosity is the resistance which a liquid exhibits to the flow of one layer over another. Although it is possible to change the shape of any liquid by the application of force, the extent of this change of shape depends greatly on the magnitude of the force and the length of time of its application and on the viscosity of the liquid. The viscosity varies greatly from materials like heavy lubricating oils, to water and to liquids of low viscosity like benzene.

The force required to slip one layer of a liquid past another with a definite velocity will depend directly on the viscosity of the liquid and on the areas exposed to each other and, inversely, on the distance separating the two surfaces.

The unit of viscosity is the *poise*, named after Poiseuille who pioneered in the study of viscosity. It is a viscosity such that, when a force of 1 dyne is applied to a region of the liquid having a surface area of 1 sq cm, it will slip past a parallel stationary region of the liquid 1 sq cm in surface area 1 cm away, with a velocity of 1 cm per second.

The viscosity η of a liquid can be determined directly in poises by passing a liquid through a tube of small diameter and making use of the following formula:*

$$\eta = \frac{P\pi r^4 t}{8vl} \tag{25}$$

where t is the time required for v ml of liquid to flow through a capillary tube of length l and radius r under an applied pressure P.

The quantitative measurement of absolute viscosity by this method is difficult. Accordingly, indirect measurements are usually made in which the viscosity of a liquid is determined relative to another liquid whose viscosity is already known. This determination of physical-chemical constants by making relative measurements and comparing them with similar measurements of a standard substance is a common procedure. The absolute measurements of the standard substance may well take years of research with expensive equipment and highly specialized techniques, whereas the relative measurements can often be made quickly and easily and with a high degree of accuracy. Moreover, an ordinary attempt to obtain absolute measurements by direct means may be frought with serious inaccuracies.

In the case of viscosities, the times required for two liquids to flow through a capillary tube may be determined under conditions where all the variables except the viscosities of the liquids are maintained the same. If a given volume of a liquid of viscosity η_1 and density d_1 takes t_1 seconds to flow through the capillary, and the same volume of a second liquid of viscosity η_2 and density d_2 takes t_2 seconds to flow through the same capillary, we have the following relation,

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

or

$$\eta_1 = \frac{d_1 t_1}{d_2 t_2}\eta_2 \tag{26}$$

From measurements of the densities and times of flow of the two liquids it is a simple matter to calculate the viscosity η_1 of the first liquid when

* The derivation of this formula is given in specialized texts such as Barr's "A Monograph on Viscometry," Oxford University Press, Oxford, 1931.

that of the second is known. Quite commonly water is taken as the reference liquid and at 25° η_2 has a value of 0.00895 poise.

An instrument used for the determination of viscosities is called a *viscometer*. Several types of viscometers are indicated in **Fig. 48.**

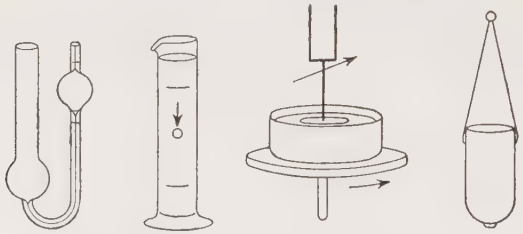


FIG. 48. Various types of viscometers.

The viscosity of a liquid may be determined by measuring not only the time required for a measured volume of liquid to flow through a capillary tube but also the time required for a heavy sphere (ball bearing) to fall through a liquid. Or two disks may be placed in the liquid and measurements made on the torsional force produced on one by the rotation of the other; or the time required for a liquid in a cup to run out through a small hole in the bottom may be determined.

The viscosity of liquids has been found to decrease about 2 per cent for each degree rise in temperature. Increase of pressure, on the other hand, causes the viscosity of liquids to increase, the change in viscosity being greater at higher pressures than at low. The viscosities of a few liquids at different temperatures are shown in Table IV.

TABLE IV

VISCOSITY OF LIQUIDS IN POISES

	0°	25°	50°	75°
Water	0.01793	0.00895	0.00549	0.00380
Ethanol	0.0179	0.0109	0.00698	.....
Benzene	0.0090	0.0061	0.0044	.....

The viscosity of an ideal gas would increase as the temperature increases. Viscosities of most liquids decrease. This fact suggests that the passage of one layer of liquid across another involves the migration from one large group of molecules to another. There is other evidence,

too, for the existence of molecular clustering in liquids. The temperature effect on viscosity permits a calculation of the energy required for molecules to break away from these groups. Attempts have been made to treat the matter mathematically.*

An empirical relation exists as follows,

$$\log \eta = \frac{A}{T} + B \tag{27}$$

where A and B are constants.

Some properties are brought out best by considering the *fluidity* ϕ which is defined as the reciprocal of viscosity. It is a measure of the tendency of the liquid to flow, whereas η is a measure of the resistance to flow. The fluidities of mixtures of nonpolar liquids are in general additive. Thus,

$$\phi = m\phi_1 + n\phi_2 \tag{28}$$

where m and n are the volume fractions of the two liquids. The viscosities of mixtures of associated liquids or liquids with large dipole moments which exhibit some interaction may give widely varying viscosities. In fact, mixtures of some liquids have viscosities greater than either pure liquid alone.

Viscosity is an important property in both practical and theoretical work. In biology and physiology the viscometer has become an almost indispensable instrument for the study of the properties of blood and other animal fluids, and in the realm of technology it has been applied successfully to the solution of a wide variety of problems presented by the paint, rubber, glue, textile, and other industries.

Viscosity is an important factor which must be considered in the design of chemical-engineering equipment, because the cost of pumping is often considerable, and these costs depend greatly on the viscosity of the liquids or gases. The data given in Table IV and the derivation of the fundamental equation itself depend on the assumption that the liquid (or gas) is flowing slowly and gently, with one hypothetical layer slipping smoothly past another. When a fluid is forced rapidly through a tube or around curves or obstacles, as in industrial absorption towers, the flow of liquid or gas changes from smooth or laminar flow to turbulent flow, and, under this condition, the viscosity may increase greatly. This increase from normal to high viscosity due to turbulence may occur rather suddenly as the velocity is increased.

* Glasstone, Laidler and Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, 1940.

REFERENCES

GLASSTONE, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York 1946, Chapter VII.

BINGHAM, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, 1922.

RIDEAL, "An Introduction to Surface Chemistry," Second Edition, Macmillan Co., New York, 1930.

WILLOWS and HATSCHEK, "Surface Tension and Surface Energy," P. Blakiston's Son & Co., Philadelphia, 1923.

PROBLEMS

1. Propene has the following vapor pressures at the following absolute temperatures:

T (°K)	150	200	250	300
p (mm)	3.82	198.0	2,074	10,040

Graph these data so as to obtain a nearly straight line, and determine the vapor pressure at 225° K. *Ans.* 740 mm.

2. In an industrial operation 10,000 cu ft of air is blown through a chamber per minute. The air at 25° and 40 per cent relative humidity is dried by removal of the water in an adsorbing agent. Calculate how many kilocalories of heat will be required per hour to regenerate the adsorbing agent by evaporating the water (582 cal per gram). The vapor pressure of water at 25° is 23.7 mm. 1 cu ft = 28.316 liters.

Ans. 90,600 kcal.

3. The heat of vaporization of ether is 88.39 cal per gram at its boiling point, 34.5°.

(*a*) Calculate the rate of change of vapor pressure with temperature dp/dT, near the boiling point.

(*b*) What is the boiling point at 750 mm?

(*c*) What is the vapor pressure at 36.0°?

Ans. (*a*) 26.5 mm per degree. (*b*) 34.1°. (*c*) 800 mm.

4. The vapor pressure of solid benzene is 2.24 mm at −30° and 24.5 mm at 0°; and the vapor pressure of liquid benzene is 26.73 mm at 0° and 118.5 mm at 30°. Calculate from these data (*a*) the melting point of benzene and (*b*) the heat of fusion of benzene. *Ans.* (*a*) 5.8°. (*b*) 2366 cal/mole.

5. From the data of the tables given in this chapter estimate the temperature at which methanol has a vapor pressure of 92.5 mm. *Ans.* 16°.

6. Methanol has a surface tension of 22.6 dynes per centimeter and a density of 0.79 at 20°. What is the radius of the largest capillary which will permit the liquid to rise 1.5 cm? *Ans.* 0.0389 cm.

7. If it takes 10 minutes to drain a capillary pipet at 25° when filled with water, how long will it take to drain it when it is filled with ethanol (density = 0.789)?

Ans. 15.4 minutes.

---

8. (*a*) How many tons of water can be evaporated from a square mile of land on a windy summer day, if it is assumed that the limiting factor is the supply of solar heat which amounts to about 1.3 cal per minute per square centimeter for a 10-hour day? The temperature is 25°, the vapor pressure of water is 23.7 mm, and the heat of vaporization 582 cal per gram. One mile = 1.609 kilometers.

(*b*) How many liters of air is required to hold this much water if the temperature is 25° and the barometer 740 mm?

---

9. Ten liters of air was bubbled through carbon tetrachloride at 20°. The loss in weight of the liquid was 8.698 g. Calculate the vapor pressure of carbon tetrachloride by the approximate formula and by the more exact formula.

10. (*a*) If 0.1 g of water is introduced into an evacuated 1-liter vessel at 100°, what will be the pressure in millimeters of mercury?

(*b*) If 10 g of water is introduced into an evacuated 1-liter vessel at 100°, what will be the pressure in millimeters of mercury?

11. A room 5 by 10 by 4 m is filled with air containing some water vapor. The temperature is 20°, and the relative humidity is 60 per cent. The vapor pressure of water at 20° is 17.36 mm. (The relative humidity is the partial pressure of water vapor divided by the vapor pressure of the liquid water.) How many grams of water are contained in the air of this room?

12. A block of ice is placed in a lake of pure water, forced 100 ft below the surface, and maintained in a quiet steady position. What will be the temperature of the surface of the ice? Assume that the densities of the ice and water are not changed by the pressure. At atmospheric pressure the melting point of ice is 0°. The densities of ice and water are 0.9106 and 1.000, respectively.

13. Calculate the vapor pressure of benzene C_6H_6 at 25° from the knowledge of the boiling point and the heat of vaporization.

14. The critical temperature of carbon tetrachloride is 283.1°. The densities in grams per ml of the liquid d_l and vapor d_v at different temperatures are as follows:

$t°$	100°	150°	200°	250°	270°	280°
d_l	1.4343	1.3215	1.1888	0.9980	0.8666	0.7634
d_v	0.0103	0.0304	0.0742	0.1754	0.2710	0.3597

What is the critical molar volume of carbon tetrachloride?

15. Acetone has a density of 0.790 and rises to a height of 2.56 cm in a capillary tube having a radius of 0.0235 cm. What is the surface tension of the acetone at this temperature?

16. Estimate (*a*) the critical temperature and (*b*) the heat of vaporization per gram of *n*-heptane C_7H_{16} from the fact that the boiling temperature is 98.4° at 1 atm. The density is 0.684. (*c*) Estimate the surface tension at 25°.

---

17. The vapor pressure of 2,2-dimethylbutanol is given by the expression,

$$\log p = \frac{-4849.3}{T} - 14.701 \log T + 53.1187$$

where p is expressed in millimeters of Hg. Calculate the heat of vaporization (*a*) at 25°, (*b*) at the boiling point, 136.7°.

18. What is the boiling point of water on a mountain where the barometer reading is 500 mm?

19. It is proposed to operate a large calcium oxide lined furnace at a temperature of 2100° C. The volatility of the calcium oxide, CaO, may be a difficulty. Air is blown continuously through the furnace at a rate of 1000 cu ft (28,320 liters) per minute (measured at 0° C and 760 mm pressure). Assuming that, if the sublimation pressure of the calcium oxide is large enough to give a loss of more than 5 kg per day, the process will be impractical, calculate the maximum permissible sublimation pressure (vapor pressure) in millimeters of the CaO, if the process is to be practical. Assume that the air becomes saturated with CaO vapor.

20. At 0° ice absorbs 80 cal per gram in melting; water absorbs 597 cal in vaporizing.
(*a*) What is the heat of sublimation of ice at this temperature?
(*b*) At 0° the vapor pressure of both ice and water is 4.6 mm. What are the rate of change of vapor pressure with temperature dp/dT for ice at this temperature?
(*c*) Estimate the vapor pressure of ice and of liquid water at −5°.

21. Liquid mercury has a density of 13.690 g per milliliter, and solid mercury has a density of 14.193 g per milliliter, both being measured at the melting point −38.87° C. The heat of fusion of Hg is 2.33 cal per gram. What are the melting points of mercury (*a*) under a pressure of 10 atm and (*b*) under 3540 atm? The observed melting point under 3540 atm is −19.9° C.

22. The boiling point of *n*-butyl chloride is 77.96°.
(*a*) Using this as the only experimental datum available, calculate the vapor pressure at 50°, and compare with that calculated from the empirically determined equation (in which p is expressed in centimeters):

$$\log p = -\frac{1763}{T} + 6.912$$

(*b*) Calculate the heat of vaporization per gram.

23. The densities of vapor and liquid methyl ether at various temperatures are as follows:

t	30°	50°	70°	100°	120°
d_l	0.6455	0.6116	0.5735	0.4950	0.4040
d_v	0.0142	0.0241	0.0385	0.0810	0.1465

If the critical temperature of this substance is 126.9°, what is its critical volume?

24. The vapor pressures of ethyl chloride are 465 mm at 0° and 760 mm at the boiling point of 12.7°. Compare the heats of vaporization as calculated by the approximate equation using increments, with the more exact values obtained by integration.

25. Estimate the critical temperature of benzene from the surface-tension data. The density of benzene at 25° is 0.879.

26. Plot log of viscosity of mercury against the reciprocal of the absolute temperature for the following data, and estimate the viscosity of mercury at 50°.

t	0°	20°	35°	98°	203°
η	0.01661	0.01547	0.01476	0.01263	0.01079

27. A certain liquid boils under atmospheric pressure (760 mm) at t°. Estimate (*a*) the critical temperature of the substance, (*b*) the heat of vaporization of liquid, (*c*) its boiling point at 720 mm pressure. How accurate would you expect these estimates to be?

28. Plot the logarithm of the vapor pressure of mercury against $1/T$ for values of T between 0° and 360° (from reference tables), and draw tangents at two different temperatures. Show that the heat of vaporization changes with the temperature. If mercury vapor is monatomic, what can be stated regarding the specific heat of liquid mercury?

29. Mercury does not wet a glass surface. Draw a figure analogous to Fig. 47 (page 184) for mercury and glass, and calculate the relative positions of the mercury surfaces, if the diameter of the capillary is 0.1 mm. The density of mercury is 13.5 g per milliliter. The surface tension of mercury is 520 dynes per centimeter.

30. Using the equation defining viscosity, determine the dimensions of viscosity in terms of the fundamental units of mass, length, and time.

31. Look up data for five typical inorganic and organic liquids, and estimate to what extent one can assume that, although the specific heats of liquids vary greatly, the heat capacity per cubic centimeter is reasonably constant.

32. Show that the observed boiling point T_0 °K at a barometric pressure of p mm may be corrected approximately to the corrected boiling point, T_{corr} °K, at 760 mm by the following equation:

$$T_{\text{corr}} = T_0 + \frac{T_0}{8000}(760 - p)$$

CHAPTER X

SOLUTIONS

A *solution* may be defined as a system of different chemical substances which has the same chemical composition and physical properties in every part. If the system is composed of only two chemical substances, it is called a *binary solution.* When sugar is added to water, for example, a solution of sugar in water is produced. The substance which is present in the larger quantity is usually called the *solvent* and the substance present in lesser quantities the *solute.* Thus, sugar is the solute dissolved in the solvent water. This designation is purely arbitrary, particularly when two liquids can be dissolved in each other in all proportions. Under such conditions either one may be regarded as the solvent.

The quantitative prediction of solubility on the basis of physical properties of the solute and solvent is possible for only a limited number of solutions. In general, it can be stated that similar substances such as benzene and toluene or alcohol and water will dissolve in each other, as well as substances which tend to interact chemically. For example, the attraction of the molecules or ions for solvent water provides the necessary energy for breaking apart the crystal lattice when certain crystals such as sugar or salts are placed in water. Substances which are not alike or which do not combine chemically generally are not very soluble in each other. For example, hydrocarbons and fats, as a rule, are insoluble in water but soluble in some organic solvents.

The Composition of Solutions. The composition of a solution can be specified in four or five different ways, each of which has advantages for a particular purpose.

Volume concentrations are used in volumetric analysis because it is convenient to introduce with each milliliter of solution a definite number of molecules. A *molar solution* contains 1 mole of solute in a liter of solution. A *normal solution* contains the combining or equivalent weight in grams of the solute dissolved in a liter of solution, but it is necessary to specify whether the solution is normal with respect to neutralization or oxidation or other reaction and to what stage the oxidation or neutralization is carried.

Weight concentrations are used in physical chemistry because they are uninfluenced by temperature, whereas the volume concentrations

are subject to variations caused by changes in density. A *molal solution* contains 1 mole of solute dissolved in 1000 g of solvent. The term "molal" and symbol "m" usually refer to weight concentrations, whereas the term "molar" and symbol "M" usually refer to volume concentrations. One may be converted into the other when the density of the solution is known.

Mole fractions are used in theoretical work because many physical properties of solutions are expressed most simply in terms of the relative numbers of molecules. The *mole fraction* N of a substance in a solution is defined as the number of moles of that substance divided by the total number of moles of all the substances comprising the solution. If a solution contains n_A moles of the substance A and n_B moles of the substance B, then, the mole fractions are defined as follows:

$$\text{Mole fraction of } A = N_A = \frac{n_A}{n_A + n_B} \tag{1}$$

$$\text{Mole fraction of } B = N_B = \frac{n_B}{n_A + n_B} \tag{2}$$

It is obvious that the mole fraction of A plus the mole fraction of B must be equal to 1. If three or more different substances are involved, the denominator always contains the total number of moles of all kinds.

Percentage by weight is often used in technical work to express the composition of a solution.

Example 1. Illustrate the four different ways in which concentrations of solutions can be expressed using a solution containing 1 mole of ethanol (46 g) in 1000 g of water, the density of the solution being 0.992.

Weight concentration:

$$\frac{1 \text{ mole}}{1000 \text{ g}} \times 1000 = 1 \text{ molal}$$

Volume concentration:

$$\frac{1 \text{ mole}}{\frac{1000 + 46}{0.992} \text{ ml}} \times 1000 = 0.948 \text{ molar}$$

Mole fractions:

$$\text{Mole fraction } H_2O = N_1 = \frac{\frac{1000}{18}}{\frac{1000}{18} + 1} = 0.982$$

$$\text{Mole fraction } C_2H_5OH = N_2 = \frac{1}{\frac{1000}{18} + 1} = 0.018$$

Percentage by weight:

$$\text{Percentage } H_2O = \frac{1000}{1000 + 46} \times 100 = 95.6$$

$$\text{Percentage } C_2H_5OH = \frac{46}{1000 + 46} \times 100 = 4.4$$

Solutions of Gases. The addition of one gas to another constitutes the simplest type of solution, in which each substance possesses the same properties after mixing as before. This case of two gases occupying the same volume might well be called a mixture, but the term solution is a broader term which includes not only simple mixtures of this type but also those cases where some physical or chemical interaction, as in the case of the dissolving sugar, is required in order to enable the molecules of both substances to spread uniformly throughout the whole volume.

With the exception of gases like hydrogen chloride and ammonia which react with each other, most gases can be mixed in any proportions, and the resulting mixture has properties which would be expected if they retained the properties which they possessed as individual gases. For example, the total pressure of a mixture of gases is equal to the sum of the partial pressures of each gas taken alone in the same volume. This is known as Dalton's *law of partial pressure*. It is expressed by the relation

$$p = p_A + p_B + p_C + \cdots \tag{3}$$

where p_A, p_B, p_C are the partial pressures of the gases A, B, C, and p is the total pressure.

Dalton's law was verified experimentally by Ramsay who placed a heated thin-walled palladium vessel containing nitrogen in a larger vessel through which hydrogen could be passed. At high temperatures the palladium walls will allow hydrogen to pass through readily but will not permit nitrogen to pass through. The pressure of the gas in the inner palladium vessel was measured with a manometer, and, when the hydrogen was swept through the outer vessel at a constant pressure, the manometer registered an increase in pressure equal to that of the hydrogen pressure. The hydrogen had passed into the inner palladium vessel exerting its full pressure, and the manometer registered the total pressure equal to the sum of the partial pressure of the nitrogen originally present, plus the partial pressure of the hydrogen added later.

It would be expected that this law would not be any more accurate than the simple gas law and that it would be subject to severe limitations at high pressure. Data regarding deviations from Dalton's law have been very meager.

Edwards and Roseveare * measured the following volume changes at 25° and 1 atm when 3174 ml of the first gas was mixed with 3421 ml of the second gas and the pressure was readjusted to 1 atm: Nitrogen + hydrogen increased 1.23 ml; carbon dioxide + hydrogen increased 2.14 ml; and ethylene + hydrogen increased 2.94 ml.

* Edwards and Roseveare, *J. Am. Chem. Soc.*, **64**, 2816 (1942).

These changes in volume provide interesting material for the direct calculation of the interattraction between molecules in one of the simplest possible chemical systems.

Ideal and Nonideal Solutions. It has been shown that an ideal gas is one in which there is no attraction between the molecules and no change in internal energy when the volume is changed. Similarly, in an ideal liquid solution there is no special force of attraction between the components of the solution, and no change in internal energy is produced on mixing. Under these conditions no change in the character of liquids is produced by mixing, merely a dilution of one liquid by the other. When two liquids are mixed to give an ideal solution, there is no heat effect, and the properties are strictly additive. The volume of the solution is the sum of the volumes of the two liquids, and there is no more shrinkage or expansion than when two different samples of the same liquid are mixed. Other physical properties of the solution, such as refractive index, fluidity, and vapor pressure, can be calculated directly by averaging the properties of the components which make up the solution.

One of the most fundamental properties of a substance is the tendency for its molecules to pass into the surrounding space. It is manifest, for example, in the vapor pressure of a liquid or solid and in solubility. In solutions this escaping tendency describes accurately the activity of the substance when surrounded by the molecules of the other substances. It is measured directly as the partial vapor pressure of the solute or the solvent in the solution. Thus, measurement of vapor pressure is of considerable importance in the study of solutions.

The vapor pressure of a pure liquid depends on the rate of escape of molecules from the surface of the liquid, and, when the liquid is mixed with another liquid, the concentration is decreased, and the rate of escape from the surface diminished. Moreover, in an ideal solution, where the character of the liquid remains unchanged, the partial vapor pressure of one component is directly proportional to the fraction of molecules of that component in the mixture. In other words,

$$p_A = \frac{n_A}{n_A + n_B} p_A{}^0 = N_A p_A{}^0 \tag{4}$$

where p_A is the partial pressure of the component A, $p_A{}^0$ is the vapor pressure of the pure substance, and $n_A/(n_A + n_B)$, or N_A, is the mole fraction of the component A. Likewise, in an ideal solution of two components the vapor pressure of the other component would be given by the expression:

$$p_B = N_B p_B{}^0$$

Example 2. The vapor pressure of pure benzene at 20° is 74.7 mm. What is the partial pressure of benzene above a solution of benzene and toluene having a mole fraction of 0.9 benzene? These two liquids form a solution which is nearly ideal.

$$0.9 \times 74.7 = 67.2 \text{ mm}$$

If there are several components present in an ideal solution, each will have a partial pressure equal to its vapor pressure in the pure state multiplied by its mole fraction in the solution.

In an ideal solution of A and B the behavior of each substance is unaffected by the presence of the other. For example, the attraction between two neighboring molecules of A, A–A, is just the same after the molecules have been dispersed through the solution, and the attraction between two neighboring molecules of B, B–B, is just the same as in pure B. Methanol, for example, forms an ideal solution with ethanol, and a given molecule behaves just the same as it did before mixing. The fraction of molecules getting to the surface where they can pass off into the vapor is equal to the mole fraction in the solution. Ideal solutions are rare. They are more likely to be found when both components are similar chemically.

In a nonideal solution there may be attraction A–B between neighboring A and B molecules which is greater than the A–A attraction or the B–B attraction. This may result in the lessening of the partial vapor pressures of A and B. Again, the presence of B molecules may cause the A–A attraction to decrease and thus increase the partial vapor pressure of A; and the presence of A may decrease the force of attraction between B and B so that the escaping tendency or vapor pressure of B is increased. These changes in the A–A and the B–B attractions may be manifested

TABLE I[1]

Partial Pressures of Benzene and Toluene in Solution at 20°

Mole Fraction Benzene	Benzene		Toluene		Total	
	$p_{obs.}$	$p_{calc.}$	$p_{obs.}$	$p_{calc.}$	$p_{obs.}$	$p_{calc.}$
0.00	0	0	22	22	22	22
0.27	18	20	17	16	36	36
0.44	34	33	12	12	47	45
0.55	41	41	11	10	51	51
0.67	49	50	8	7	57	57
1.00	75	75	0	0	75	75

[1] Bell and Wright, J. *Phys. Chem.*, **31,** 1884 (1927).

as heat effects or volume changes or abnormalities in viscosity, surface tension, and other properties of the solution, but the vapor-pressure change is usually regarded as the most significant of the physical measurements.

The exact interactions of A–A, B–B, and A–B have not been worked out quantitatively yet, but the general principles of electrostatic attractions between ions, dipoles, and induced dipoles discussed on pages 39 and 40 seem to be well established.

In Tables I, II, and III three different types of solutions are illustrated. The partial vapor pressures can be obtained experimentally by the gas-

TABLE II[1]

PARTIAL PRESSURES OF ACETONE AND CHLOROFORM IN SOLUTION AT 35.2°

Mole Fraction Chloroform	Chloroform		Acetone		Total	
	$p_{obs.}$	$p_{calc.}$	$p_{obs.}$	$p_{calc.}$	$p_{obs.}$	$p_{calc.}$
0	0	0	344	344	344	344
0.2	34	59	270	275	304	334
0.4	82	117	183	207	265	324
0.6	148	177	102	137	250	314
0.8	225	236	42	67	267	303
1.00	293	293	0	0	293	293

[1] Zawidzki, *Z. physik Chem.*, **35**, 129 (1900).

TABLE III[1]

PARTIAL PRESSURES OF ACETONE AND CARBON DISULFIDE IN SOLUTION AT 35.2°

Mole Fraction CS_2	Carbon Disulfide		Acetone		Total	
	$p_{obs.}$	$p_{calc.}$	$p_{obs.}$	$p_{calc.}$	$p_{obs.}$	$p_{calc.}$
0	0	0	344	344	344	344
0.2	280	102	290	275	570	377
0.4	378	206	255	204	633	410
0.6	425	306	230	138	655	444
0.8	460	410	190	67	650	477
1.00	512	512	0	0	512	512

[1] Zawidzki, *Z. physik Chem.*, **35**, 129 (1900).

saturation method, in which a known volume of air or other gas is passed slowly through the solution, and the two liquids are vaporized in ratios corresponding to their vapor pressures. The mixed vapors are then condensed from the gas stream and analyzed with a refractometer. The partial vapor pressures $p_{obs.}$ are determined for each liquid. The sum of the two gives the total $p_{obs.}$. The calculated partial pressures $p_{calc.}$ are calculated by multiplying the vapor pressure of the pure liquid by its mole fraction in the solution. The data are given in the tables and shown graphically in **Figs. 49, 50,** and **51.** The broken lines give the value of $p_{calc.}$.

One of the types of interaction leading to nonideal solutions is that in which a "hydrogen bond" (described on page 38) can be formed, making the *A–B* attraction greater than the *A–A* or the *B–B* attraction. Examples of this hydrogen bonding are found when proton acceptors, which contain the double-bond oxygen as in acetone or other ketones or in acetic acid or other carboxylic acids, are mixed with proton donors such as NH groups or $CHCl_3$. When there is a possibility of such hydrogen bonding between the different compounds, the solution will probably be nonideal, and the partial pressure of the two components will probably be less than the calculated value, as is the case for acetone and chloroform. According to this reasoning, carbon tetrachloride and acetone should give a more nearly ideal solution than chloroform and acetone.

The benzene–toluene solution is an ideal solution in which the molecules of the two substances are much alike, and the experimentally determined pressures agree with the calculated partial and total pressures.

In the acetone–chloroform solution the observed values are considerably less than the calculated values. The acetone molecules are held back in solution by the chloroform molecules more than by other acetone molecules; and the chloroform molecules are held back more by the acetone molecules. This mutual attraction is to be expected in view of the fact that an actual chemical compound $(CH_3)_2CO \cdot CHCl_3$ is formed, which indeed can be isolated. With many other substances the mutual attraction caused, at least in part, by an attraction between dipoles or between dipoles and induced dipoles, is sufficient to produce nonideal solutions and yet insufficient to give a recognizable chemical compound between the two.

The acetone–carbon disulfide solution is typical of those solutions which give abnormally large vapor pressures—the molecules require less energy to get into the gas phase than when surrounded by molecules of their own kind.

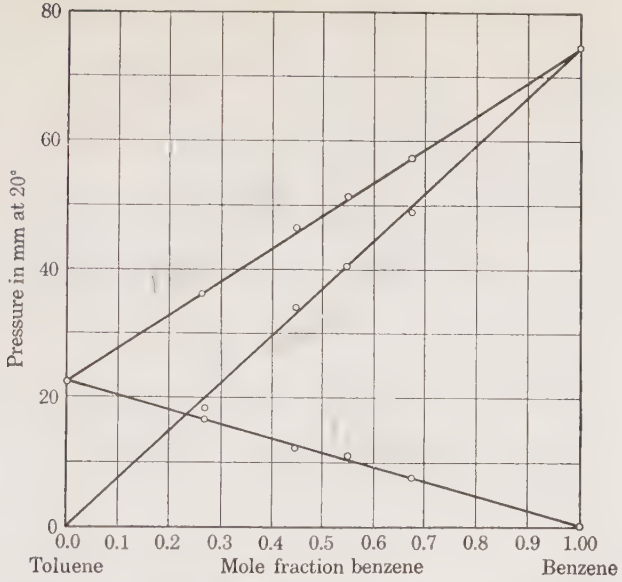


FIG. 49. Partial vapor pressures of toluene–benzene solutions illustrating an ideal solution.

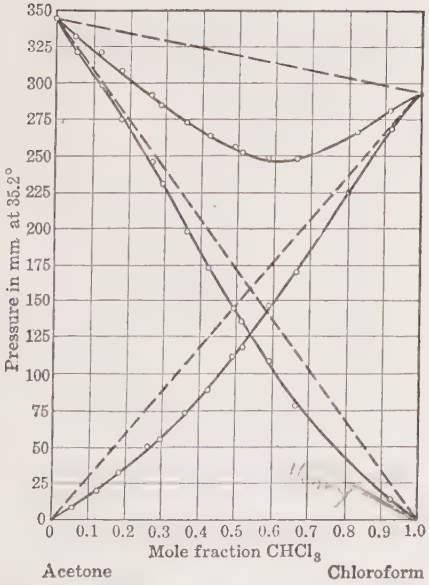


FIG. 50. Partial vapor pressures of solutions of acetone and chloroform showing pressures less than those calculated for an ideal solution.

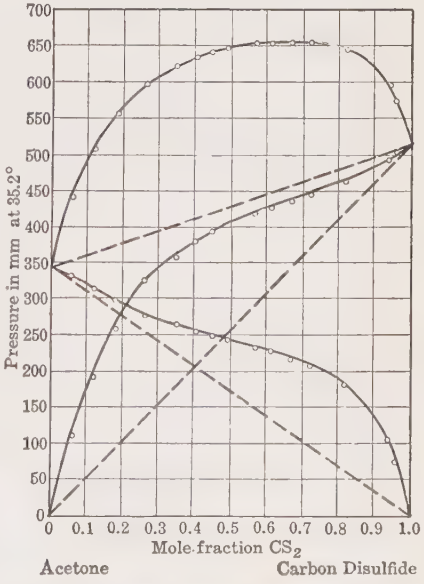


FIG. 51. Partial vapor pressures of solutions of acetone and carbon disulfide showing pressures greater than those calculated for an ideal solution.

Raoult's Law and Henry's Law. The simple relation expressed in equation 4 was discovered empirically in 1884 by Raoult for a solvent containing small quantities of solute. The solute is so dilute that the solvent is but slightly affected. *Raoult's law* may be expressed as follows:

$$p_{\text{solvent}} = p^0_{\text{solvent}} N_{\text{solvent}} \qquad (5)$$

According to this law, the partial vapor pressure of the solvent is equal to the vapor pressure of the pure solvent multiplied by the mole fraction of the solvent in the solution.

Henry's law applies to the solute.

$$p_{\text{solute}} = KN_{\text{solute}} \qquad (6)$$

The partial vapor pressure of the solute is proportional to the mole fraction of the solute. This equation is distinctly different from Raoult's law in that the proportionality constant K is not the vapor pressure of the pure solute but a constant which must be evaluated experimentally for each solution. The difference lies in the fact that the solute is diluted to such an extent that its properties may be quite different from those of the solute in its pure state. Raoult's law applies to the solvent in solutions so dilute that the properties of the solvent are not greatly different from those of the pure solvent.

In an ideal solution Henry's law, as well as Raoult's, is an exact law, and equation 6 becomes identical with equation 4. Moreover, the proportionality constant K becomes identical with the vapor pressure of the pure solute.

In nonideal solutions the value of K in Henry's law is determined by measuring the vapor pressure of the solute in dilute solutions at known mole fractions. Then,

$$K = \frac{p_{\text{solute}}}{N_{\text{solute}}} \qquad (7)$$

and the same values of K should be obtained from data at different mole fractions. In practice, the law is not exact, and the properties of the dissolved solute, including its escaping tendency, change as the concentration changes.*

Solutions of Gases in Liquids. When a dissolved substance evaporates into a closed space, the concentration of its molecules increases, and the rate at which these molecules return to the solution increases

* If the "constant" K changes, the most significant value to take is the one obtained by plotting a few values of p/N against N for the solute and extrapolating it to infinite dilution as shown on page 279. The intercept of the curve at $N = 0$ gives the value of K to be taken for theoretical calculations.

until a dynamic equilibrium is attained. The partial pressure in the gas space under these conditions is the partial vapor pressure of the solute in solution. The solute can be a permanent gas just as well as a liquid or a solid, and it then seems more natural to look at the phenomenon as the solution of a gas in the solvent rather than as the solute escaping from the solution to give a definite vapor pressure. However, equation 6 is still applicable; in fact, it was while studying the solubility of gases in liquids that Henry discovered this relationship.

The solubilities of a few gases are given in Table IV in terms of Henry's constant K in which the concentration of molecules in the gas phase,

TABLE IV

Solubility of Gases at 25°

$$K = \frac{p_A}{N_A} = \frac{\text{pressure of gas } A \text{ in millimeters}}{\text{mole fraction gas } A \text{ in solution}}$$

Gas	Solvent	
	Water	Benzene
H_2	5.34×10^7	2.75×10^6
N_2	6.51×10^7	1.79×10^6
O_2	3.30×10^7	
CO	4.34×10^7	1.22×10^6
CO_2	1.25×10^6	8.57×10^4
CH_4	31.4×10^6	4.27×10^5
C_2H_2	1.01×10^6	
C_2H_4	8.67×10^6	
C_2H_6	23.0×10^6	

expressed in millimeters of pressure, is divided by the concentration of the gas in solution expressed in mole fractions.

Sometimes the solubilities are expressed in terms of Bunsen coefficients, which give the number of liters of gas reduced to 0° and 760 mm pressure which will dissolve in 1 liter of the solvent under a pressure of 760 mm at a specified temperature.

Example 3. Express the solubility of carbon dioxide in water at 1 atm pressure and 25° in terms of moles n per liter, assuming that the liter of solution contains practically 1000 g of water

$$K = 1.25 \times 10^6 = \frac{760}{n_{CO_2}} \left(n_{CO_2} + \frac{1000}{18.02} \right)$$

The number of moles of carbon dioxide n_{CO_2} may be considered negligibly small in comparison with the number of moles of water, 1000/18.02. Then,

$$n_{CO_2} = \frac{760 \times 55.55}{1.25 \times 10^6} = 3.38 \times 10^{-2} \text{ moles per liter}$$

The Bunsen solubility coefficient for carbon dioxide may be calculated from this value, giving

$$\frac{3.38 \times 10^{-2} \times 22.41}{1} = 0.757$$

As a first approximation, the volume of gas which dissolves is independent of the pressure above the solution, because the number of moles of dissolved gas changes directly as the pressure, and the volume of the gas above the solution changes inversely as the pressure.

Henry's law, like most of the laws of solutions, is not exact except in very dilute solutions. Up to a pressure of 1 atm it holds within 1 to 3 per cent with many gases.

Dalton showed that the solubility of the individual gases in a mixture of gases is directly proportional to their partial pressures, the solubility of each gas being nearly independent of the presence of the others. The solubility of oxygen in water is nearly twice as great as that of nitrogen, and, since the solubility of one gas is unaffected by the presence of the other, the dissolved air is considerably richer in oxygen than the air above water.

The theoretical explanations of the solubility of inert gases in liquids have not yet been developed. A few empirical facts regarding the subject will be helpful in eventually formulating a satisfactory theory:

(*a*) The order of increasing solubility of gases in a liquid usually remains the same in different liquids.

(*b*) The increase in volume caused by the solution of a mole of the gas in a solvent is nearly equal to the corresponding value of b in the equation of van der Waals.

(*c*) The solubility of a gas in liquids is usually decreased by an increase in temperature. There are numerous exceptions, however, especially with the solvents liquid ammonia, molten silver, and many organic liquids.

(*d*) The solubility of gases in water is usually decreased by the addition of other solutes, particularly electrolytes. The extent of this "salting out" varies considerably with different salts, but with a given salt the relative decrease in solubility is the same for different gases. For example, if a certain salt reduces the solubility of oxygen in water to 80 per cent of its value, it will also reduce the solubility of nitrogen in water to about 80 per cent of its value.

The solubility of the unreactive gases is probably caused by an attractive force between the solute molecules and the solvent molecules due to dipole-induced dipoles (page 40), more generally referred to as van der Waals' forces. Even though a molecule is electrically neutral as a whole, there are parts of the molecule that are positively charged and other parts that are negatively charged, as indicated by the existence of a dipole moment. These electrically charged parts are able to induce electric charges of the opposite sign in molecules which are in the immediate neighborhood. For example, helium molecules can certainly have no unbalanced electric forces, and the attractive force due to electric dipoles which they induce in each other is so weak that it is overcome by the slight thermal agitation which exists at 4° K, the boiling point of helium. Water molecules, on the other hand, have a considerable dipole moment, and, although the molecule as a whole is neutral, the charged parts induce an opposite charge in a neighboring molecule, and a force of attraction is set up between the two, causing some helium to be dissolved in water.

A similar example is found in the solubility of butane in water. The supposedly inert butane molecule has been found to form a solid hydrate with water. This unexpected phenomenon was a technical problem in the passage of moist butane gas through pipes in cool weather.

The solubility of gases and other solutes is affected by the addition of large quantities of salts. Sometimes the salting-out effect can be explained on the hypothesis that it is caused by the hydration of the salt. A portion of the water combines with the salt, and the water which is thus removed from the role of solvent is no longer free to absorb gas. More specifically, one can consider that the water molecules with their electric dipoles are partially oriented with respect to the ions or dipoles of the dissolved salt and are less free to induce dipoles in the molecules of gas.* Sometimes the salts interact with solute as, for example, the salting in of hydrochloric acid which leads to a greater solubility.

It is common observation that a glass of cold water, when warmed to room temperature, shows the presence of many small air bubbles. The rate of escape of the molecules of dissolved gas from the liquid is increased more by an increase in temperature than is the rate at which molecules of the gas phase strike the surface and dissolve in the liquid leading to a decreased solubility. From an energy standpoint, the forces of attraction which cause the gas molecules to crowd into the liquid are partially offset by the increased kinetic energy at the higher temperatures.

* The influence of salting out on the dipole of a second substance has been measured by Williams and Albright, *Trans. Faraday Soc.*, **33**, 247 (1937).

Vapor Composition of Binary Systems. If an ideal solution could be found composed of two liquids with identically the same vapor pressure at a given temperature, the composition of the vapor would be the same as that of the liquid. But, if one of the components has a higher vapor pressure than the other, it will be present in excess in the vapor, even when there are the same number of molecules of each in the liquid, that is, at mole fraction such that $N_A = N_B = 0.5$. In fact, at all mole frac-

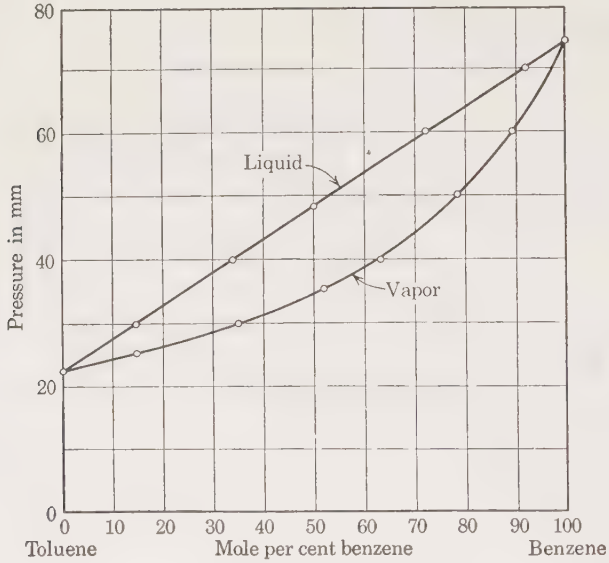


FIG. 52. Vapor pressure–composition graph at constant temperature for an ideal solution, toluene and benzene.

tions the vapor will be richer than the liquid in the more volatile component. The same general considerations apply to solutions which are not ideal, but in these solutions the partial pressures cannot be calculated with exactness from the mole fractions.

In **Fig. 52** the total vapor pressure of an ideal solution, benzene in toluene, is plotted against the mole per cent of the component which has the higher vapor pressure. The temperature is constant. There must be two curves, one for the liquid and one for the vapor composition, because the composition of the two is generally not the same at a given pressure. The line shown in Fig. 52 for the vapor pressure plotted against the composition of the liquid is straight because the solution is ideal. Ideal solutions are comparatively uncommon. The vapor-pressure curve for *n*-hexane in benzene at constant temperature, shown in **Fig. 53,** is a more common type of diagram. Because the partial pres-

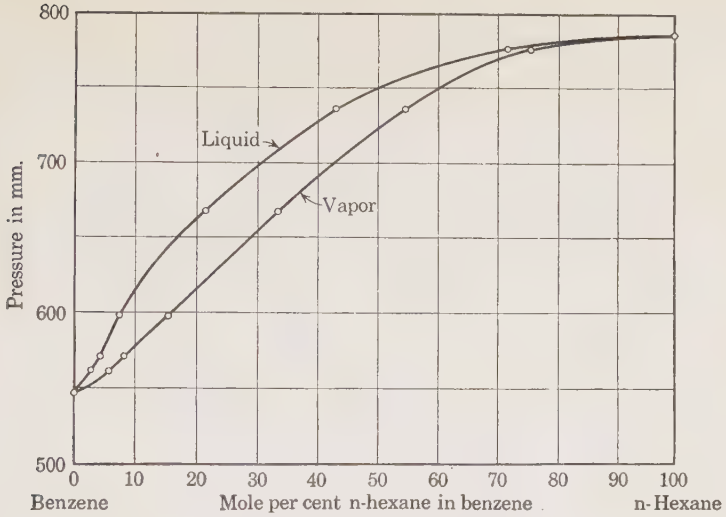


FIG. 53. Vapor pressure–composition graph at constant temperature for a nonideal solution, *n*-hexane and benzene.

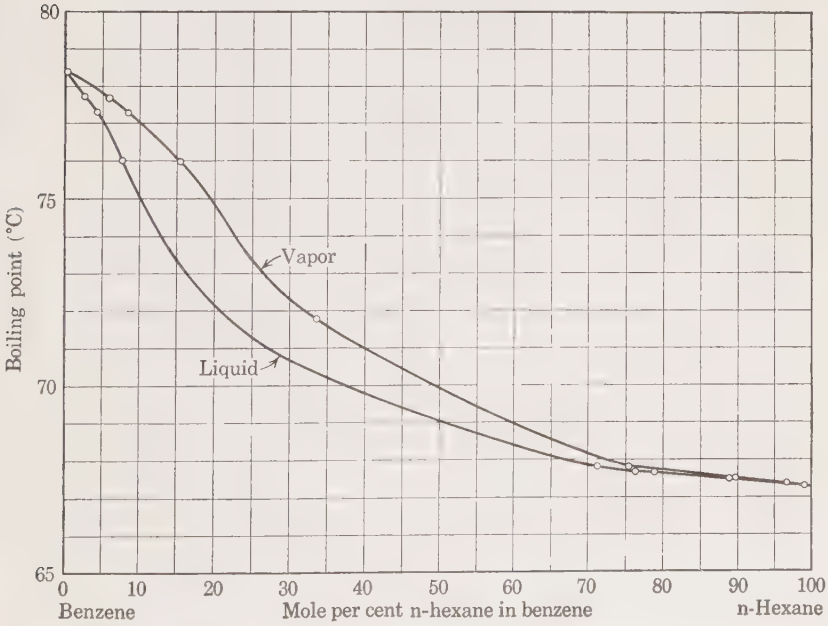


FIG. 54. Temperature–composition graph at constant pressure for a nonideal solution, *n*-hexane and benzene.

sures are not proportional to the mole fraction (or mole per cent), the liquid curve is no longer straight.

The curve for the liquid in Fig. 53 gives the total vapor pressure exerted by a liquid of the composition given on the x axis. The curve for the vapor gives the pressure at which vapors of a specified composition first show a tendency to form a liquid phase.

Since the vapor is relatively richer in the more volatile component, it follows that the curve representing vapor composition must always lie closer to the component which has the higher vapor pressure. For example, in Fig. 53, since n-hexane is seen to have a higher vapor pressure than benzene, the vapor curve must lie nearer to the side corresponding to n-hexane than does the curve which gives the composition of the liquid.

More often the boiling temperatures (the temperature at which the total pressure becomes equal to the atmospheric pressure) are plotted against the mole per cent, as shown in **Fig. 54** for n-hexane and benzene at 735 mm.* The liquid with the higher vapor pressure (hexane) has the lower boiling point, and the whole appearance of the curves is reversed. Since the vapor is relatively richer in the more volatile component, the vapor curve lies closer to the pure component having the lower boiling point, that is, closer to the pure n-hexane.

Maximum and Minimum Boiling Points. In some cases, the departure from ideal behavior is so great that the curves exhibit actual maxima as shown in **Fig. 55** for acetone and chloroform at 750 mm.

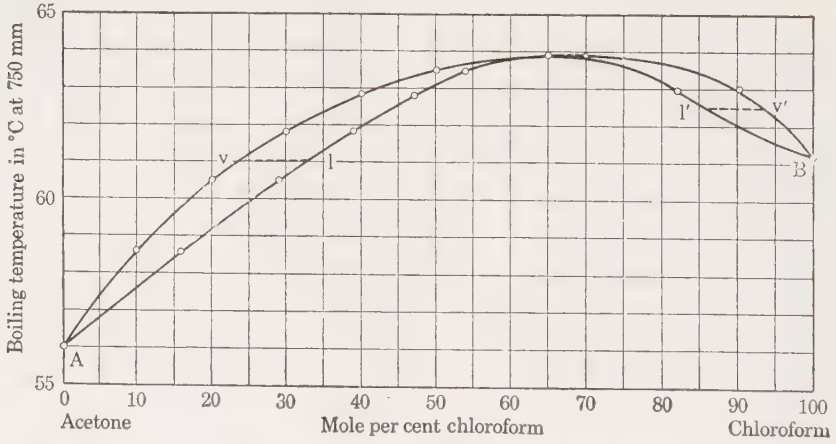


FIG. 55. Temperature–composition graph for acetone and chloroform showing a maximum.

It may be remembered that this system has a minimum in the total vapor-pressure curve as shown in Fig. 50. These maxima and minima

* Tongberg and Johnston, *Ind. Eng. Chem.*, **25**, 734 (1933).

fall at the same composition in both curves (except for slight changes due to the differences in temperature).

Many pairs of liquids are known whose boiling-point curves pass through a minimum, as shown in **Fig. 56** for ethanol in benzene. The

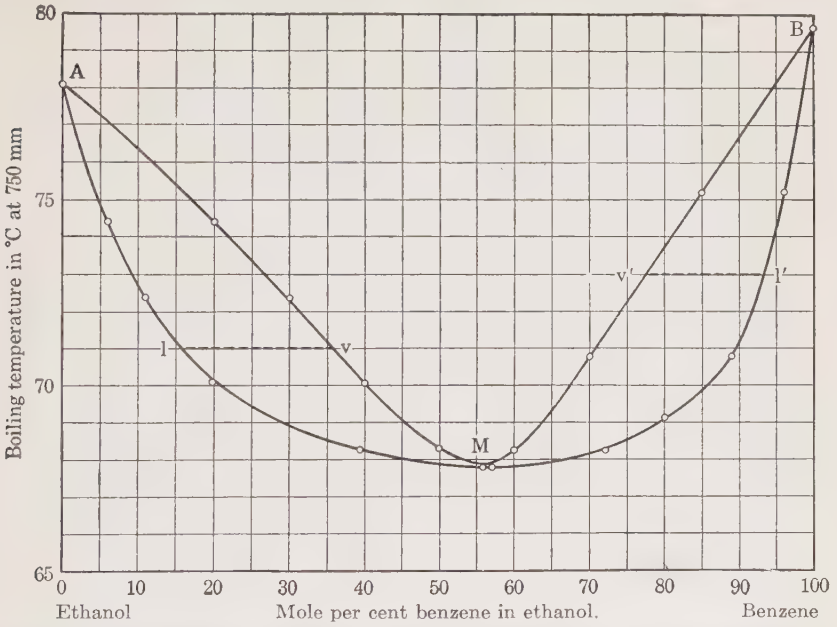


FIG. 56. Temperature–composition graph for ethanol and benzene showing a minimum.

vapor-pressure curves would pass through a maximum at the same composition. Typical solutions exhibiting maxima and minima in the boiling point curves are given in Tables V and VI.

TABLE V

BINARY MIXTURES WITH MAXIMUM BOILING POINTS

Components	Pressure, mm	Maximum Boiling Point	Weight, per cent
Hydrochloric acid + water	760	108.58°	20.222 hydrochloric
	700	106.42	20.360 hydrochloric
	600	102.21	20.638 hydrochloric
Nitric acid + water	760	120.5	68.0 nitric
Acetic acid + water	760	107.1	77.9 acetic
Chloroform + acetone	760	64.5	65.5 chloroform
Phenol + cyclohexanol	760	182.5	90.0 phenol

TABLE VI

Binary Mixtures with Minimum Boiling Points

Components	Pressure, mm	Minimum Boiling Point	Weight, per cent
Ethanol + water	760	78.13°	95.57 ethanol
Carbon tetrachloride + methanol	760	55.70	44.5 carbon tetrachloride
Carbon disulfide + acetone	760	39.25	61.0 carbon disulfide
Ethyl acetate + water	500	59.4	92.46 ethyl acetate

A very complete list of liquids giving maximum and minimum boiling points is now available.*

Maxima and minima are not confined to vapor-pressure and boiling-point curves, but they are sometimes found when freezing points, densities, viscosities, heats, and other properties are plotted against composition. *They are not found in ideal solutions.* Whenever a maximum exists, there must be at least two opposing factors, one tending to increase the magnitude of the property and the other tending to decrease it as the concentration is changed.

The mixture of hydrochloric acid and water has been studied extensively, and the composition of the constant-boiling mixture is so reproducible that it is used as a standard in quantitative analysis. If any solution of hydrochloric acid is boiled for a sufficient time under a pressure of 760 mm, the temperature will gradually rise to 108.58 and remain stationary, and the mixture boiling at this constant temperature will contain 20.222 per cent hydrochloric acid by weight.

In the case of hydrochloric acid and water, the minimum in the vapor-pressure curve, or maximum in the boiling-point curve, is due to the ionization of hydrochloric acid. Water and pure hydrochloric acid have high vapor pressures, but the electrically charged hydrogen and chloride ions cannot escape from the solution. It is shown in the next chapter that they lower the vapor pressure of the water. In small amounts, hydrochloric acid added to water lowers the vapor pressure through its ions; but in large amounts, it increases the vapor pressure by adding to the solution the more volatile hydrochloric acid molecules, a fact which can be realized from the sharp odor of hydrochloric acid in the concentrated solutions.

* Horsley, Table of Azeotropes and Non-Azeotropes, *Anal. Chem.*, **19**, 508–600 (1947)

It was thought at one time that maxima of this type correspond to definite chemical compounds, and indeed a maximum in a freezing-point composition does indicate the formation of a chemical compound, as explained in a later chapter. The composition of 20.22 per cent HCl in the constant-boiling mixture corresponds very closely to the formula $HCl \cdot 8H_2O$, but the relation is accidental. It has been proved that such mixtures are not definite chemical compounds since the composition of the distillate changes when the distillation is carried out under different pressures, as shown in Tables V and VI. Usually, these maxima do not come at compositions corresponding to any chemical formula, and, if maxima in two different properties occur in the same mixture, they often occur at different compositions.

Chemical combination or attraction due to the existence of dipoles or induced dipoles in the molecule is, nevertheless, a factor in many solutions. The tendency for two liquids to attract each other in a loose compound through the formation of a hydrogen bond is responsible for the formation of binary systems with a minimum vapor pressure and maximum boiling point, particularly if the vapor pressures are fairly close together. Supporting this view, Ewell and Welch * have shown that most of the ketones form with alkyl halides boiling-point curves which have maxima, if the boiling points are close together.

Distillation of Binary Systems. When binary or two-component systems are distilled under constant pressure, three types of boiling-point curves can be distinguished, as shown in Figs. 54, 55 and 56.

The lower-boiling-point component (or mixture of components in minimum-boiling mixtures) is present in relatively greater amount in the vapor phase in all these diagrams in which boiling temperatures are plotted along the y axis.

When binary mixtures which exhibit a maximum in their boiling-point curves, as shown in Fig. 55, are vaporized the more volatile component comes off in greater amount than the liquid mixture as shown at l–v and l'–v'. The boiling point of the remaining liquid then rises until the liquid phase acquires the composition corresponding to the maximum, at 65.5 per cent of chloroform in Fig. 55. The liquid and vapor then have the same composition, and distillation proceeds without further change in composition, provided the pressure remains constant. Such a solution which distils without a change in composition or temperature is called an *azeotropic solution.*

A constant-boiling temperature does not necessarily show that the liquid is a pure compound. Such a criterion for purity of an organic liquid should be supplemented with other tests.

* Ewell and Welch, *J. Am. Chem. Soc.*, **63**, 2475 (1941).

Similarly, if a mixture having an initial composition which corresponds to l' is distilled, the liquid phase becomes relatively less rich in chloroform and finally acquires the composition of the mixture having the maximum boiling point.

From all solutions with more than 65.5 mole per cent, pure chloroform can be separated in the distillate by successive distillations, but pure acetone cannot be obtained. The ultimate residue will contain 65.5 mole per cent chloroform and 34.5 per cent acetone. Pure acetone can be obtained in the distillate however by successive distillations of solutions which contain less than 65.5 mole per cent chloroform.

The third type of boiling-point curve has a minimum, as shown in Fig. 56, for ethanol and benzene. Any mixture whose composition lies between that of A and M may be separated by fractional distillation. Pure A is then left in the residue, and the mixture M, having the composition of the minimum boiling point, is obtained as the distillate. In like manner, mixtures whose composition lies between those of B and M can also be separated by fractional distillation into pure B and the mixture M. Pure B, however, cannot be obtained on distilling a mixture whose composition lies between that of A and M. As shown in Fig. 56, the vapor compositions v and v' are nearer to the minimum boiling composition than the corresponding liquid compositions l and l'.

Fractional Distillation. When a mixture of two liquids vaporizes, that component which has the higher partial vapor pressure tends to concentrate in the vapor, thus producing a difference in composition between the liquid and the vapor which is in equilibrium with it. This vapor may be condensed, and the vapor coming from this condensate is still further enriched in the more volatile component. This successive vaporization and condensation is called fractional distillation.

The situation is represented in **Fig. 57*a*** for a simple binary mixture in which there is no maximum nor minimum in the boiling curve. Although the data of the figure are only for one pressure, data at other pressures give similar curves. The dotted line which makes an angle of 45° with the x axis is such that any point on it has the same value along the x and y axes; in other words, the composition of vapor and liquid along this hypothetical line is the same. The full line along y_1 and y_3 gives the composition of vapor plotted along the y axis corresponding to any composition of liquid plotted along the x axis. If the mixture has a minimum vapor pressure as in Fig. 50, the curve intersects the 45° line with a maximum slope as shown in **Fig. 57*b***. If the mixture has a maximum, as in Fig. 51, it intersects with a minimum slope as shown in **Fig. 57*c***. In Fig. 57*a*, there are two points where the composition of vapor and liquid is the same, namely, pure A and pure B. In Figs.

57*b* and *c* there is a third point where they are the same, namely, at the maximum or minimum boiling point.

The process of fractional distillation may be illustrated by reference to Fig. 57*a*. If one starts with a large amount of liquid of composition x_1 and evaporates a small portion, the vapor will be found to have the composition y_1. If all this vapor is condensed, the condensed liquid will have the composition y_1 also. If the composition of the condensed liquid is called x_2, it follows that $x_2 = y_1$. When a very small portion of

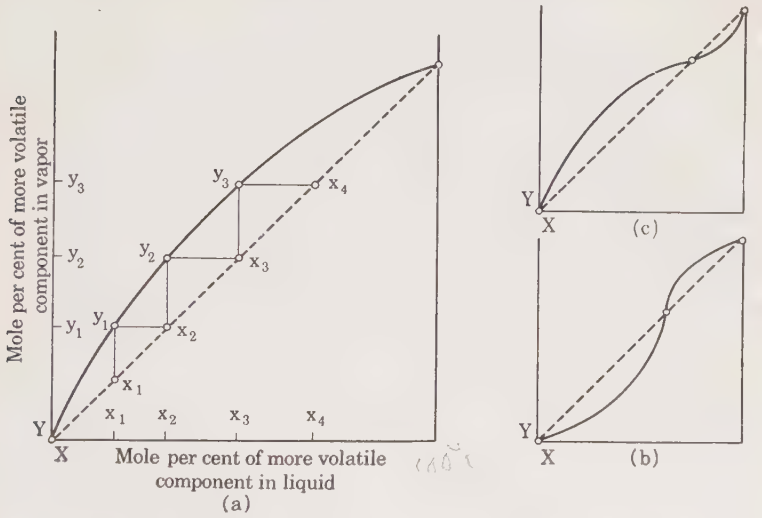


FIG. 57. Fractional-distillation diagrams used in calculation of the number of theoretical plates in a fractionating column: (*a*) simple solution; (*b*) solution with minimum in vapor-pressure curve; (*c*) solution with maximum in vapor-pressure curve.

this liquid of composition x_2 is evaporated, the vapor will have the composition y_2. If this process of evaporation and condensation is continued, it is possible to obtain a very small amount of the more volatile component in a practically pure state.

A series of successive vaporizations and condensations may be carried out in a fractionating column, without the material having to be transferred from boiler to condenser at every step. The simplest form to visualize is the tower of bubble caps diagrammed in **Fig. 58.**

When all the condensed vapor is returned to the boiling liquid under conditions of total reflux, fresh liquid of constant composition corresponding to composition x_1 of Fig. 57 is fed in at the bottom through the reservoir and valve, and vapor from it bubbles out through the liquid in the first or lowest trough. The composition of this liquid cor-

responds to y_1 or x_2. The vapor from the first layer of condensed liquid now corresponds to y_2, and it passes up through the second bubble cap where it is condensed to give the second layer of liquid having composition x_3 which is equal to that of y_2. The overflow is returned to the first layer and eventually down to the residue. The process is continued through a whole series of liquid layers. Each layer is called a

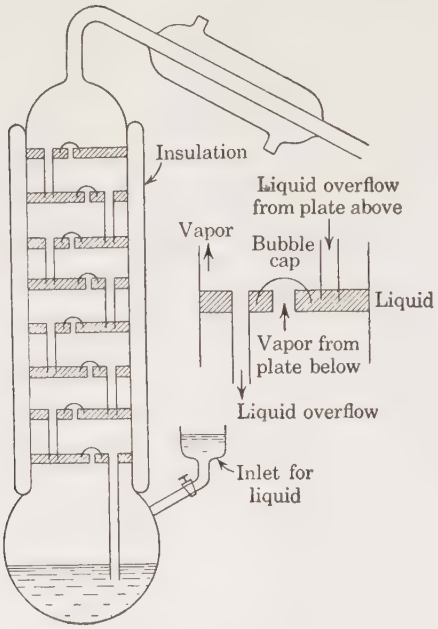


FIG. 58. Bubble-cap fractionating column.

plate. The distillate at the top is greatly enriched in the more volatile component, some enrichment taking place at each condensation and evaporation, that is, at each plate.

The column is well insulated, or it is surrounded by a controlled heating jacket so that there will not be general condensation on the walls. The whole system reaches a state of equilibrium in which the composition of liquid on each plate remains unchanged. In actual practice, for continuous distillation the incoming liquid is fed into the tower near the middle.

In the laboratory, distillations are usually carried out in batches, and the liquid in the bottom is gradually reduced in volume as the vapor at the top is distilled out and recovered by condensation. The mathematical analysis under these conditions is more complicated, but, if the

column is operated at nearly total reflux, so that very little of the vapor is distilled out, a state of equilibrium is reached which is practically the same as that described for the continuous-flow operation.

The bubble-cap towers are not often used, because it is simpler to pack the tower with material which will provide efficient contact between liquid and vapor and will occupy only a small volume so that there is free space to permit a large through-put of vapor. Helices of glass, spirals of screen, and various types of packing * are used with varying degrees of efficiency.

The efficiency of a column is expressed in terms of the number of theoretical plates to which it is equivalent. A *theoretical plate* may be considered as a hypothetical section of the distilling column of such length that the vapor leaving at the top of the section has had opportunity to come into equilibrium with the liquid leaving at the bottom of the section. It may be visualized as the equivalent of a layer in a 100 per cent efficient bubble-cap tower, that is, one in which the vapor leaving the plate is in complete equilibrium with the circulating liquid on the plate.

The number of theoretical plates in a column at infinite reflux can be determined by finding the composition of the exit vapors and that of the liquid in the distilling flask under conditions of total reflux, marking these two points on the 45° line of Fig. 57*a* and finding the number of horizontal–vertical steps which can be drawn between the two compositions. Thus, if the composition of the distillate is found to be x_4 and that of the residue to be x_1, three steps can be drawn connecting the two. Since the distilling pot itself corresponds to one theoretical plate, the column to which this example applies has two theoretical plates.

A fractionating column operating at total reflux obviously would not be very practical for separating liquids, but the higher the reflux ratio, that is, the greater the ratio of liquid returned to the distilling flask to the vapor distilled out, the greater is the efficiency of separation. An ordinary distilling flask and unpacked column may be equivalent to one or two theoretical plates, but, when it is well packed, with special packing which presents a large area of the flowing liquid to the vapor, it is possible to have the equivalent of a theoretical plate every inch or so. Fractionating columns of 10 to 20 theoretical plates operating at a reflux ratio of 10 to 1 effectively separate liquids which have boiling points so close together that they cannot be separated in a simple distillation flask.

* Daniels, Mathews, and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1941; Morton, "Laboratory Techniques in Organic Chemistry," McGraw-Hill Book Co., New York, 1939, Chapter IV.

Marked improvements have been made recently in laboratory distillations and purifications, as well as in industrial distillations. The demands of the petroleum industry have given an impetus to the development of the theory and practice of fractional distillation.

Immiscible Liquids. The vapor-pressure relations of two immiscible liquids are shown in **Fig. 59.** Each exerts its own vapor pressure independently of the other. The total vapor pressure is obviously the sum of the vapor pressures of the two liquids if neither liquid dissolves in the

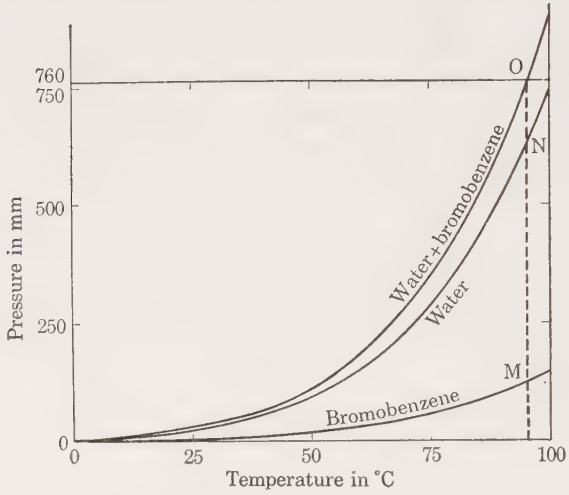


FIG. 59. Pressure temperature graph for immiscible liquids, water and bromobenzene.

other, and the vapor pressure and composition of the vapor are constant at constant temperature, independent of the composition of the liquid mixture.

In the example shown, the total vapor pressure reaches atmospheric pressure O at 95°, and both liquids distil together at this temperature. When either one of the liquids has completely distilled away at this temperature, the vapor pressure drops to that of the remaining liquid, M or N.

Since the pressure of a gas is proportional to the number of molecules in a given space, the vapor pressures are represented by p_A and p_B and the number of moles by n_A and n_B for the two immiscible substances A and B. Then,

$$\frac{p_A}{p_B} = \frac{n_A}{n_B} \tag{8}$$

The number of moles can be calculated by dividing the weight in grams by the molecular weight, giving

$$\frac{p_A}{p_B} = \frac{w_A/M_A}{w_B/M_B}$$

or

$$\frac{w_A}{w_B} = \frac{p_A M_A}{p_B M_B} \tag{9}$$

This formula is useful in calculating the relative weights w_A and w_B of the two liquids which are condensed out in distillation.

A common laboratory and industrial operation which makes use of this relation is *steam distillation*. The steam is blown through a liquid which is immiscible with water, and the condensing steam carries with it quantities of the other liquid.

If an organic substance is immiscible with water and unaffected chemically by steam, it is possible to effect a purification by steam distillation, even though the vapor pressure is relatively low. It is the low molecular weight and the cheapness of water which render it so suitable for distillations of this kind.

Example 4. How many grams of water would be required to steam-distil a kilogram of bromobenzene? The vapor pressure of bromobenzene is 125 mm at 95°, and that of water is 635 mm.

$$\frac{p_{H_2O}}{p_{C_6H_5Br}} \times \frac{M_{H_2O}}{M_{C_6H_5Br}} = \frac{635}{125} \times \frac{18}{157} = \frac{w_{H_2O}}{1000}. \qquad w_{H_2O} = 584 \text{ g}$$

The behavior of partially miscible liquids is similar to completely miscible liquids as long as there is only one liquid layer, showing that the two liquids dissolve completely in each other. When the mutual solubility is exceeded and two layers are formed, the vapor-pressure relations resemble those of the immiscible liquids.

Partial Molal Quantities. The concept of partial molal quantities, developed by G. N. Lewis, has helped materially in placing the study of solutions on an exact basis. For example, when a mole (32 g) of methanol is added to a small quantity of water, the change in volume produced on mixing is not the same as when it is added to a large quantity of water. The volume depends on the concentration, and, since the concentration changes during the mixing, the measurements are complicated in a manner which was not realized in the early work on solutions. This problem can be solved readily with the methods of partial

differentiation by determining the change produced by the addition of an infinitesimal quantity of the solute. The partial molal volume $\overline{V}$ is defined by the equation

$$\overline{V} = \frac{\partial V}{\partial n} \tag{10}$$

where n is the number of moles. In words, it is the rate of change in volume produced by the addition of solute to the solution at constant temperature and pressure. The partial molal volume of the solute $\overline{V}_2$ changes with the concentration, and it can be visualized as the increase in volume produced by adding 1 mole of the solute to a large quantity of the solution, a quantity so large in fact that the addition of the 1 mole of solute does not increase appreciably the concentration of the solution. For example, a mole of methanol weighs 32.03 g and occupies 40.45 ml. When it is added to a large reservoir of pure methanol, the volume is increased 40.45 ml, but, when it is added to a large reservoir of a solution containing 0.2 mole fraction of methanol and 0.8 mole fraction of water, the increase is only 37.7 ml. An obvious method for determining the partial molal volume of a solute consists in plotting the volume of the solution against the number of moles of solute contained in 1000 g of the solvent (that is, against the molality), and determining the slope of the curve as shown in **Fig. 60.** The slope of the curve $\partial V/\partial n_2$ at any molality gives the rate of change in volume with the moles of solute added, and this is by definition the partial molal volume of the solute. In Fig. 60 the tangent is drawn to the curve at a molality of 13.35, and it is found to have a slope of (1625 − 1375)/(16.30 − 9.60) or 37.3, which is the partial molal volume of the methanol at this molality.

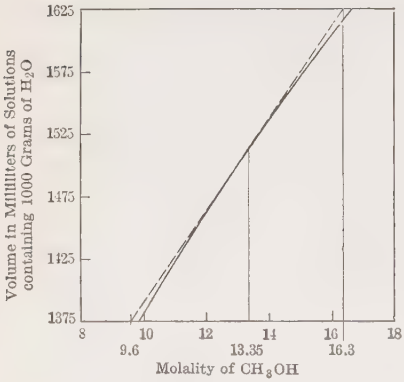


FIG. 60. Determination of partial molal volumes by the method of tangents.

The partial molal volume of water is determined in a similar manner by drawing tangents to the curve obtained by plotting the molal volume of the solution against the molality of the water in the methanol–water solution.

Other specialized graphical methods are available for obtaining partial molal quantities with greater precision than can be obtained by this

simple graphical determination of tangents.* Sometimes calculated quantities are plotted in such a way that the errors of graphing apply only to a correcting term rather than to the whole quantity.

Other properties such as partial molal free energy or partial molal heat capacities or partial molal enthalpies may be determined in the same way as the partial molal volumes. The partial molal free energy $\overline{F}$ of a given component is an important quantity which is used in deriving formulas for the thermodynamic behavior of solutions because it has the same value in every phase which is in equilibrium.

After the partial molal volumes (or other properties) have been determined, the volume of the whole solution can be obtained at any concentration by direct addition, as shown by equation 11,

$$n_1\overline{V}_1 + n_2\overline{V}_2 + n_3\overline{V}_3 + \cdots = V \tag{11}$$

where V is the volume of the whole solution, and where n_1, n_2, n_3, etc., refer to the number of moles of the different components and $\overline{V}$ to the corresponding partial molal volumes.

Heat of Solution. The heat effect which accompanies the dissolving of a mole of solute is known as the *molal heat of solution*. It changes with the concentration all the way from an infinitely dilute solution, that is, pure solvent, to a saturated solution as is illustrated in **Fig. 61.** This figure gives the heat absorbed when n_2 moles of sodium bromide is dissolved in 1000 g of solvent.† The addition of 1 mole of this solute to 1000 g of water absorbs 800 cal of heat, and it might be expected that the addition of 2 moles to 1000 g of solvent would absorb 1600 cal. However there is an interaction of the solute ions with the solvent which gives a heat effect that usually is not directly proportional to the amount of solute added. In concentrated solutions, the solvent molecules behave quite differently from those in the pure solvent, and, of course, there is an interaction between solute molecules when the concentration is large. In sodium bromide, shown in Fig. 61, the addition of 2 moles of solute to 1000 g of solvent absorbs 1390 cal, the addition of 3 moles absorbs 1790 cal, and the addition of more solute gives a continuously decreasing absorption of heat per mole dissolved. When the solution becomes saturated at 9.0 molal, the further addition of solute produces no further effect because no more can dissolve.

The integral heat of solution is defined as the heat absorbed when 1 mole of solute is dissolved in a sufficient quantity of the solvent to give the specified concentration. In Fig. 61, the integral heats of solution at 1,

* Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, page 38.

† Harned and Crawford, *J. Am. Chem. Soc.*, **59**, 1903 (1937).

2, and 3 molal are, respectively, 830, $\frac{1390}{2}$ or 695, and $\frac{1790}{3}$ or 597. It is possible also to calculate the heat absorbed when a given number of moles is added to a solution of specified concentration. Thus, in Fig. 61, the addition of 1 mole of solute to 1 mole of solute in a 1-molal solution absorbs 1390 − 830 or 560 cal of heat.

The partial molal or differential heat of solution is defined as $d(\Delta H) \div dn_2$, where ΔH is the heat of solution of n_2 moles of solute in 1000 g

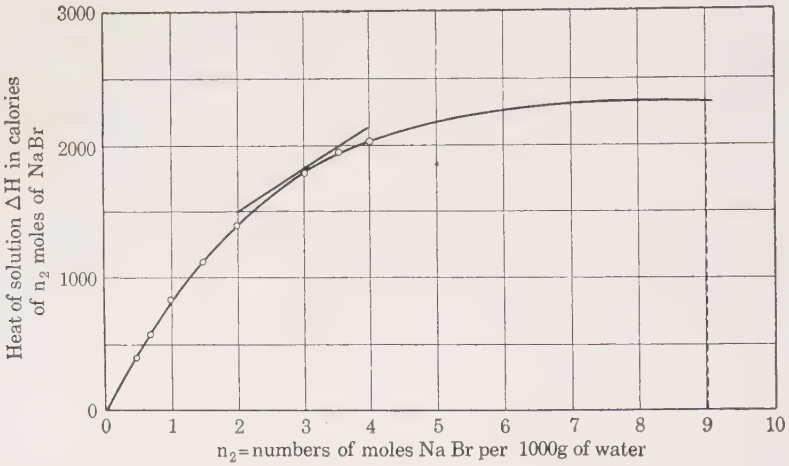


FIG. 61. Integral and differential heat of solution of sodium bromide in water.

of solvent. It is the heat of solution of a mole of solute in a quantity of solution so large that the addition of the one more mole of solute does not change appreciably the concentration of the solution. It is illustrated by the tangent at 3.0-molal solution, which has a value of 330 cal per mole. The average heat of solution obtained by dividing differences in ΔH by the corresponding differences in n is not definite. It depends on the range of concentrations which is covered. Before these methods of differential calculus were applied to solutions, confusion existed, and different investigators reported different heats of solution.

The partial molal heat of solution in the pure solvent is the limiting slope of the curve as n_2 approaches zero. It represents the heat absorbed when a mole of solute is dissolved in an infinitely large amount of pure solvent to form an infinitely dilute solution. For sodium bromide at infinite dilution $d(\Delta H)/dn_2 = 830$ cal per mole. The slope of the curve when n_2 is the molality of the saturated solution, represents the heat absorbed when a mole of solute is dissolved in a large amount of nearly saturated solution.

The integral heats of solution are recorded for a number of solutes in Table VII. They give values of ΔH when 1 mole of the substance is dissolved in the number of moles of water specified—usually 200. When ΔH is positive, heat is absorbed; when it is negative, heat is evolved.

TABLE VII

Integral Heats of Solution in Water at 20°

Solute	Moles H_2O	ΔH, kcal/mole	Solute	Moles H_2O	ΔH, kcal/mole
H_2SO_4	200	−17.7	NaCl	200	1.3
HNO_3	200	− 7.5	KCl	200	4.4
HCl	200	−17.4	KBr	200	5.0
HBr	200	−20.0	KI	200	5.1
HI	200	−19.2	$CuSO_4$	800	−15.9
NaOH	200	−10.0	$CuSO_4 \cdot 5H_2O$	800	2.8
$NaNO_3$	200	5.0	HCOOH	49	0.30
KNO_3	200	8.5	CH_3COOH	30	0.1
NH_4NO_3	200	6.3	CCl_3COOH	500	2.7
NH_4Cl	200	3.9	CH_3OH	19	2.0

Usually, heat is absorbed when a crystalline salt dissolves, because in the solution process the atoms or ions are torn apart from each other in the crystal lattice. If this process is not offset by other processes, it might be expected that as much heat would be absorbed as is absorbed in the fusion of the crystal. In fact, the heat of solution of a substance in a solvent to give an ideal solution is exactly equal to the heat of fusion. Combinations with the solvent can evolve heat which partially or wholly offsets this cooling effect.

The importance of this attraction of the solvent for the solute in the process of solution may be illustrated by the dissolving of sodium chloride. In the crystal lattice of sodium chloride, positive sodium ions and negative chloride ions attract each other strongly. The energy that is required to separate them is so great that nonpolar solvents like benzene or carbon tetrachloride will not dissolve sodium chloride; but a solvent like water, which has a large dielectric constant and a large dipole moment, combines with the ions and in so doing evolves a large amount of heat. In this way, the large energy required for breaking up the crystal lattice is made available. With sodium chloride the heat of interaction with the solvent just about offsets the heat of separation of the ions, and there is very little heat effect. With some substances the combination

with the solvent more than offsets the energy required to separate the units of the solute, and heat is actually evolved.

When a solution is diluted by the addition of more solvent, there is a heat change corresponding to the difference in the integral heat of solution at the two concentrations. As the dilution is increased, the thermal effect produced by the addition of more solvent becomes less and less and ultimately approaches zero.

The previously unpublished data of Professor T. F. Young of the University of Chicago presented in Table VIII give unusually exact in-

TABLE VIII

HEATS OF SOLUTION AND DILUTION OF SODIUM CHLORIDE IN WATER AT 25°

ΔH in calories for n_1 H_2O + n_2 NaCl = solution containing n_1 H_2O + n_2 NaCl

Molality	$\frac{n_1}{n_2}$	$\frac{\Delta H}{n_2}$	$\frac{d(\Delta H)}{dn_2}$	$\frac{d(\Delta H)}{dn_1}$	$\frac{\Delta H}{\text{Kg } H_2O}$
0.0000	∞	923	923	−0.0000	0.00
0.0100	5551	962	979	−0.0029	9.62
0.0225	2467	977	997	−0.008	21.98
0.0400	1388	989	1009	−0.015	39.56
0.0900	617	1004	1018	−0.023	90.4
0.1600	347	1008	1009	−0.002	161.3
0.2500	222.0	1005	986	+0.086	251.2
0.3600	154.2	994	952	0.27	357.8
0.4900	113.3	977	909	0.61	478.7
1.0000	55.51	898	737	2.90	898
1.9600	28.32	750	471	9.80	1470
3.2400	17.13	597	280	18.5	1934
4.0000	13.88	532	235	21.4	2128
4.8400	11.47	480	244	21.6	2323
5.7600	9.64	448	318	13.5	2580
6.0025	9.25	443	350	10.1	2659

formation regarding the heat of solution and heat of dilution for sodium chloride over a wide range of concentrations. It is interesting to note that there is a change of sign in the heat of dilution as the solution becomes dilute.

REFERENCES

HILDEBRAND, "Solubility of Non-electrolytes," Reinhold Publishing Corp., New York, 1936.

ROBINSON and GILLILAND, "The Elements of Fractional Distillation," McGraw-Hill Book Co., New York, 1939.

PROBLEMS

1. A solution of KNO_3 contains 192.6 g of salt per liter of solution. The density of the solution is 1.1432. Calculate the concentration in terms of (*a*) molality, (*b*) molarity, (*c*) mole fraction, (*d*) weight per cent.

Ans. (*a*) 2.004. (*b*) 1.905. (*c*) 0.0348. (*d*) 16.85.

2. In an evacuated vessel of 6-liter capacity, 1.0 g of water and 1.0 g of hexane are evaporated and heated to 350°.

(*a*) What is the total pressure in atmospheres?

(*b*) What is the mole fraction of water in the vapor?

(*c*) What is the percentage composition (by weight) of the vapor?

Ans. (*a*) 0.577 atm. (*b*) 0.828. (*c*) 50.

3. Exactly 1.100 g of carbon dioxide was introduced into a 1-liter flask which contained some pure oxygen before being subjected to partial evacuation. The flask was warmed to 100° and the pressure found to be 608 mm Hg. Considering oxygen and carbon dioxide to be the only gases present, calculate the weight of oxygen in the flask. *Ans.* 0.0351 g.

4. At 20°, 1 volume of water absorbs 0.03405 volume of oxygen under atmospheric pressure and 0.01696 volume of nitrogen under atmospheric pressure. When air (20.9 per cent oxygen and 79.1 per cent nitrogen by volume) is dissolved in water under atmospheric pressure, what is the percentage (by volume) of oxygen and of nitrogen in the dissolved gases?

Ans. $O_2 = 34.65$; $N_2 = 65.35$ per cent by volume.

5. The solubilities of carbon monoxide and nitrous oxide in water are 0.757 and 0.539, respectively, where solubilities are expressed in volume of gas under standard conditions per volume of solution. The solubility of carbon monoxide in 1.0 molal $Mg(NO_3)_2$ is 0.559. Calculate the solubility of nitrous oxide in 1.0 molal $Mg(NO_3)_2$. The experimental value is 0.385. *Ans.* 0.398 volume per volume of solution.

6. Ethanol and methanol form a solution which is nearly ideal. The vapor pressure of ethanol is 44.5 mm, and that of methanol is 88.7 mm at 20°. (*a*) Calculate the mole fraction of methanol and ethanol in a solution obtained by mixing 100 g of each. (*b*) Calculate the partial pressures and the total vapor pressure of the solution. (*c*) Calculate the mole fraction of methanol in the vapor.

Ans. (*a*) $N_{CH_3OH} = 0.590$; $N_{C_2H_5OH} = 0.410$.
(*b*) $p_{C_2H_5OH} = 18.25$; $p_{CH_3OH} = 52.32$; $p_{total} = 70.6$.
(*c*) 0.741.

7. Prove that, for ideal solutions of two volatile liquids A and B,

$$P = p_A + p_B = p^\circ_A + N_B(p^\circ_B - p^\circ_A)$$

Check this equation against a graph for the total vapor pressure of an ideal solution.

8. The vapor pressure of the immiscible liquid system diethylaniline–water is 760 mm at 99.4°. The vapor pressure of water at that temperature is 744 mm. How many grams of steam are necessary to distil over 100 g of diethylaniline?

Ans. 562 g.

---

9. Ten grams of pure acetic acid $HC_2H_3O_2$ is dissolved in 100 g of water. The density of the solution at 20° is 1.0123. Calculate the concentration of acetic acid in terms of (*a*) per cent by weight, (*b*) molality, (*c*) molarity, (*d*) mole fraction.

10. It has been established that the refractive index of a solution of carbon tetrachloride in benzene is a linear function of the mole fraction of either component. For benzene, $n_D^{18} = 1.5024$. For carbon tetrachloride, $n_D^{18} = 1.4618$. Calculate the

per cent by weight of CCl_4 in a solution of the two having a refractive index at 18° of 1.4807.

11. At 25° and 1 atm pressure, the solubility of oxygen, O_2, in water is 0.001225 mole per liter. How many grams are dissolved in a lake which is 1 mile in diameter with an average depth of 20 ft, if complete equilibrium with the air is assumed?

12. Benzene and toluene form a solution which is nearly ideal. At 80° the vapor pressures of benzene and toluene are as follows: vapor pressure of benzene = 753 mm Hg; vapor pressure of toluene = 290 mm Hg. In a solution containing 0.5 mole fraction of benzene and 0.5 mole fraction of toluene, what is the composition of the vapor at 80°?

13. From the data given below construct a complete temperature-composition diagram for the system ethanol–ethyl acetate. The data apply to 760 mm. A solution containing 0.8 mole fraction of ethanol EtOH is distilled completely at 760 mm. (*a*) What is the composition of the first vapor to come off? (*b*) Of the last drop of liquid to evaporate? (*c*) What would be the values of the above quantities if the distillation were carried out in a cylinder provided with a piston so that none of the vapor could escape?

N_{ethanol} liquid	N_{ethanol} vapor	*Temperature*	N_{ethanol} liquid	N_{ethanol} vapor	*Temperature*
0	0	77.15	0.563	0.507	72.0
0.025	0.070	76.7	0.710	0.600	72.8
0.100	0.164	75.0	0.833	0.735	74.2
0.240	0.295	72.6	0.942	0.880	76.4
0.360	0.398	71.8	0.982	0.965	77.7
0.462	0.462	71.6	1.00	1.0000	78.3

14. The boiling point of the immiscible liquid system naphthalene–water is 98° under a pressure of 733 mm. The vapor pressure of water at 98° is 707 mm. Calculate the per cent of naphthalene in the distillate.

15. When 1 mole of water was added to an infinitely large amount of an aqueous methanol solution having a mole fraction methanol 0.40, the volume of the solution increased 17.35 ml. When 1 mole of methanol was added to such a solution, the volume increased 39.01 ml. Calculate the volume of a solution containing 0.40 mole of methanol and 0.60 mole of water.

16. Plot enough of the data of Table VIII to determine graphically the partial molal heat of solution of sodium chloride in 0.8 molal sodium chloride solution.

17. The integral heat of solution of 1 mole of H_2SO_4 in n moles of water is given by the formula:

$$\Delta H_{\text{solution}} = \frac{-17{,}860n}{n + 1.798} \text{ cal}$$

Calculate ΔH for the following reactions:

(*a*) Solution of 1 mole of H_2SO_4 in 5 moles of water.

(*b*) Solution of 1 mole of H_2SO_4 in 10 moles of water.

(*c*) Solution of 1 mole of H_2SO_4 in a large excess of water, 100,000 moles for example.

(*d*) Addition of a large excess of water to a solution containing 1 mole of H_2SO_4 in 10 moles of water.

(*e*) Addition of 5 moles of water to a solution containing 1 mole of H_2SO_4 in 5 moles of water.

---

18. Ten grams of carbon tetrachloride (density = 1.595) and 50 g of benzene (density = 0.878) are mixed. Calculate the composition of the mixture in terms of

(*a*) per cent by weight of each compound, (*b*) mole fractions, (*c*) molal concentration, and (*d*) molar concentration, considering the benzene to be the solvent, assuming for this calculation that the solution is ideal.

19. Three flasks are connected by stopcocks. Given the following data:

Flask	*Volume* (liters)	*Contents*	*Pressure* (atm)
A	1	O_2	2
B	2	N_2	1
C	3	H_2	3

Calculate (*a*) total pressure, (*b*) partial pressure of each gas, and (*c*) mole fraction of each gas after the stopcocks are opened and the gases are mixed at constant temperature.

20. A 10-liter tank of methane at 740 mm total pressure and 25° contains 1 liter of water. How many grams of methane is dissolved in the water?

21. The reduction in solubility of gases such as carbon dioxide in aqueous solutions by inorganic salts is, within experimental errors, an additive function of ion concentrations. Using this fact, calculate, from the following data, the solubility of carbon dioxide in a 0.1 *M* solution of sodium nitrate at 25°. The solubilities are expressed in terms of volume of gas measured at 0° and 760 mm per volume of solution at 25°. The salts are dissociated into ions such as K^+ and Cl^- (page 250).

Data at 25°

Solution	*Solubility* CO_2
Pure H_2O	0.7567
0.1 *M* KCl	0.7432
0.1 *M* NaCl	0.7379
0.1 *M* KNO_3	0.7501

22. At 25° the vapor pressures of chloroform and carbon tetrachloride are 199.1 and 114.5 mm, respectively. If the two liquids form an ideal solution, (*a*) what is the composition of the vapor in equilibrium with a mixture containing 1 mole of each; (*b*) what is the vapor pressure of the mixture?

23. For mixtures of benzene and isopropanol the following data are available at 25°. Draw a complete pressure–composition diagram including partial pressure curves for each of the constituents. What would be the approximate composition of distillate obtained by distilling a liquid whose mole fraction (with respect to isopropanol) was 0.521 until its mole fraction had become 0.70? The vapor pressure of pure benzene at 25° is 94.4 mm.

Mole fraction of isopropanol		*Partial pressure of isopropanol in mm*
In liquid	In vapor	
0.000	0.000	....
0.059	0.123	12.9
0.146	0.205	22.4
0.362	0.255	27.6
0.521	0.288	30.5
0.700	0.365	36.4
0.836	0.470	39.5
0.926	0.635	42.2
1.000	1.000	44.0

24. Calculate the partial molal volume of zinc chloride in 1 molal $ZnCl_2$ solution using the following data:

Per cent by weight of $ZnCl_2$	2	6	10	14	18	20
Density, g per ml	1.0167	1.0532	1.0819	1.1275	1.1665	1.1866

25. Using the following data for cadmium nitrate in water plot the total heats of solution, $\Delta H_{\text{int.}}$ against the molality m, and determine the differential heat of solution of cadmium nitrate in a 4 molal solution.

m (molality)	1.063	1.799	2.821	4.251	6.372	9.949
$\Delta H_{\text{int.}}$ (joules)	−34.2	−56.7	−88.3	−126.0	—174.4	−228.5

26. The dissolved air described in Problem 4 is expelled by boiling into an evacuated space. When this mixture of 34.65 per cent oxygen and 65.35 per cent nitrogen by volume is redissolved in water at 20° under atmospheric pressure, what is the composition of the dissolved gas?

27. Two 2-liter vessels are connected with a tube and stopcock of negligible volume. Initially the first bulb contains 10 g of water and is at 10°. The other bulb contains 5 atm of NH_3 and is at 0°. Calculate the total pressure in the system when the stopcock is opened and the whole apparatus is brought to equilibrium at 25°. The solubility of NH_3 in water at 25° is 27.011 moles per 1000 g H_2O. Neglect second-order effects.

28. In the system isopropyl ether–isopropanol the vapor and liquid have the following compositions of isopropyl ether:

Mole Fraction Isopropyl Ether

In liquid	0	0.084	0.19	0.44	0.66	0.75	0.78	0.88	0.95	100
In vapor	0	0.30	0.45	0.64	0.73	0.76	0.78	0.84	0.91	100

Plot the data, and state whether this system exhibits a minimum or maximum boiling point. If so, which? What is the composition of this mixture of maximum or minimum boiling point? With a rough sketch show what the temperature–composition diagram would look like.

CHAPTER XI

SOLUTION OF NONVOLATILE SOLUTES

When only one of the components in a liquid system is volatile, as in an aqueous solution of sugar, both the measurements and the theoretical calculations are simplified. The total pressure of the system gives at once the partial pressure of the volatile component. The solute or solutes play no part in the measurements except insofar as they affect the escaping tendency, that is, the vapor pressure, of the solvent. Because the vapor pressure is lowered, the boiling point is raised and the freezing point is lowered. The phenomenon of osmosis is connected also with the lowering of the vapor pressure. All four of these properties are interrelated, and they are used for calculating molecular weights and other properties of dissolved substances.

From a kinetic point of view, the lowering of the vapor pressure may be explained as due to solute molecules reducing the effective concentration of the solvent. Accordingly, it is the number of molecules or separate units, rather than their kind, which determines the extent of the vapor-pressure lowering.

Lowering of the Vapor Pressure. Raoult's law is the fundamental formula for connecting the concentration of the solute with the vapor pressure of the solvent. In fact, Raoult first applied it to the lowering of the vapor pressure by various nonvolatile solutes and expressed it in the statement that the lowering of the vapor pressure divided by the vapor pressure of the pure solvent is equal to the mole fraction of the solute.

As given in the last chapter, the equation,

$$p_{\text{solvent}} = N_{\text{solvent}}\, p^{0}_{\text{solvent}} \qquad (1)$$

is applicable to ideal solutions, but the equation holds well for nonideal solutions also if they are dilute, because the solvent is only slightly changed from its normal behavior by the addition of a small amount of solute to it.

The difference between two quantities often can be determined experimentally more accurately than the absolute value of one of them. According to this principle, the difference between the vapor pressure of the solutions and that of the pure solvent can be determined and cal-

culated much more easily and accurately than the vapor pressure of the solution. Writing equation 1 in the equivalent form for the solvent, we have

$$p = N_1 p^0 = \frac{n_1}{n_1 + n_2} p^0$$

where p is the vapor pressure of the solution (or rather the partial pressure of the solvent in solution), p^0 is the vapor pressure of the pure solvent and n_2 is the number of moles of solute; n_1 is the number of moles of solvent, and N_1 is the mole fraction of the solvent in the solution. By rearranging terms it can be shown that

$$\frac{p^0 - p}{p^0} = \frac{n_2}{n_1 + n_2} = N_2 \qquad (2)$$

where N_2 is the mole fraction of the solute.

Example 1. Raoult * found that, when 2.47 g of ethyl benzoate was dissolved in 100 g of benzene at 80°, the vapor pressure was lowered from 751.9 to 742.6 mm. Calculate the molecular weight M_2 of ethyl benzoate from these data. The molecular weight of benzene is 78.1.

$$\frac{p^0 - p}{p^0} = \frac{n_2}{n_2 + n_1}$$

$$\frac{751.9 - 742.6}{751.9} = \frac{\dfrac{2.47}{M_2}}{\dfrac{2.47}{M_2} + \dfrac{100}{78.1}}$$

$$M_2 = 154$$

The molecular weight obtained by adding together the atomic weights is 150.2. If the solution were more dilute, its behavior would be more nearly ideal, and the calculated value would check better with the correct value.

The molecular weight may be calculated as well by equation 1 as by equation 2, but the mathematical operations must be carried out with greater precision. Thus, with a slide rule the calculation by equation 1,

$$742.6 = \frac{\dfrac{100}{78.1}}{\dfrac{100}{78.1} + \dfrac{2.47}{M_2}} \times 751.9$$

may give for M_2 a value anywhere between 130 and 180. However, with a five-place logarithm table the calculation gives 154, as obtained by equation 2.

* Raoult, *Z. physik Chem.*, **2**, 371 (1888).

This problem illustrates the desirability, when possible, of applying calculations to a small correcting term, as is done with equation 2, rather than to the whole quantity as is done with equation 1.

The vapor pressures of the solution may be determined by static methods in which the pressure is read directly with a manometer. A differential manometer is convenient for measuring the difference between the vapor pressure of the solution and that of the pure solvent, one arm of the manometer being connected with the solution and the other with the solvent. An oil or other liquid of low density is used as the manometer liquid, and the difference in vapor pressure is read directly on the manometer. Both liquids must be boiled out to remove any dissolved air which might later lead to an abnormal pressure.

In another method a solution containing a nonvolatile solute in one dish is allowed to come to equilibrium with a solution of a standard substance, such as potassium chloride, in another dish.* The two are placed in an enclosed thermostated vessel until there is no further loss or gain of weight, and, then, it is known that both solutions have the same vapor pressure. The concentration of the potassium chloride under these equilibrium conditions is determined with a refractometer, or by other means, and its vapor pressure is calculated from a previously determined relation between the vapor pressure and the concentration. The vapor pressure of the solution which is being measured is equal to the calculated vapor pressure of the potassium chloride solution; and the concentration of solute in the first solution is determined by chemical or physical analysis.

The gas-saturation method described on page 173 is suitable also for determining the vapor pressure of solutions. The loss in weight of the solution is determined after bubbling through a known volume of an inert gas, or the vaporized solvent is caught in an absorption tube and weighed or titrated. Again, more accurate results can be obtained with a differential method, because errors involving the absolute measurements of volume, temperature, and other variables tend to cancel out. The measurements are made first on the pure solvent and then on the solution. Accurate measurements have been made with this method on the lowering of the vapor pressure of the solvent caused by addition of the solute.†

Elevation of the Boiling Point. Since the vapor pressure of a solvent is lowered by the addition of a nonvolatile solute, it is obvious that the solution must be heated to a higher temperature than the solvent in

* Robinson and Sinclair, *J. Am. Chem. Soc.*, **56**, 1830 (1934).

† Washburn and Heuse, *J. Am. Chem. Soc.*, **37**, 309 (1915).

order that both may have the same vapor pressure. This fact is shown in **Fig. 62** where the curve for the vapor pressure of the solution is seen to cut the line of barometric pressure at a higher temperature than does the curve representing the vapor pressure of the solvent. If p is the pressure (760 mm) at which both the solvent and the solution boil, T_1 is

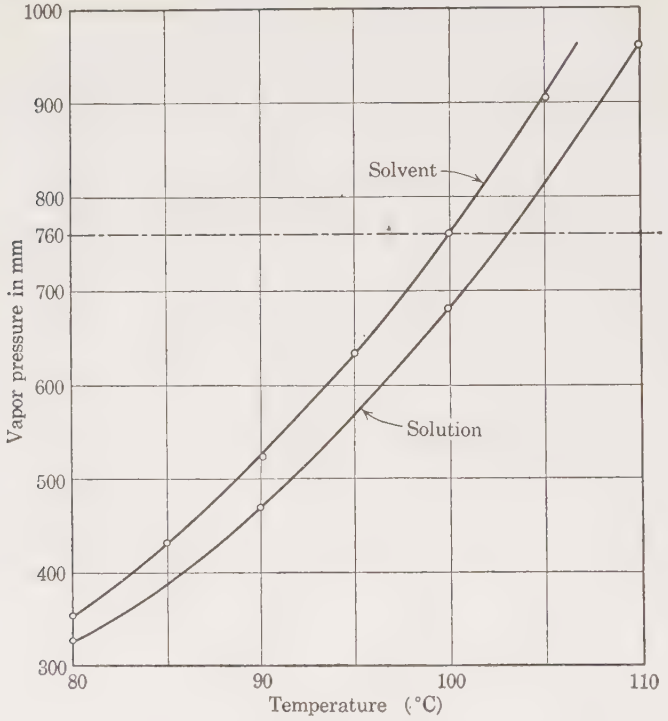


FIG. 62. Elevation of boiling point of a solvent by the addition of a nonvolatile solute—a 2.56 molal solution of sodium chloride in water.

the boiling temperature of the solvent at this pressure, and T_2 the boiling point of the solution.

This elevation of the boiling point $T_2 - T_1$ or ΔT_b is directly connected with the change in the vapor pressure p and, accordingly, with the change in concentration of the solution.

By the Clausius–Clapeyron equation (page 177),

$$\frac{dp}{dT} = \frac{p\Delta H_{\text{vap.}}}{RT^2} \qquad (3)$$

where $\Delta H_{\text{vap.}}$ is the heat of vaporization per mole.

For small changes,

$$\Delta T = \frac{RT^2}{p\Delta H_{\text{vap.}}} \Delta p \tag{4}$$

and, by Raoult's law (taking p as the vapor pressure of the solvent),

$$\frac{\Delta p}{p} = \frac{n_2}{n_1 + n_2}$$

Then,

$$\Delta T = \frac{RT^2}{\Delta H_{\text{vap.}}} \times \frac{n_2}{n_1 + n_2} \tag{5}$$

In dilute solutions the change in boiling point is so small that ΔT may be substituted for the differential dT in equation 3, but it must be remembered that the resulting formula cannot be used over large concentration ranges. Also, in dilute solutions, n_2 is negligible in comparison with n_1. For example, the neglect of n_2 in the denominator of equation 5 causes an error of 1.8 per cent in a 1-molal aqueous solution. Thus, equation 5 becomes

$$\Delta T_b = \frac{RT^2}{\Delta H_{\text{vap.}}} \times \frac{n_2}{n_1} \tag{6}$$

Since

$$\frac{n_2}{n_1} = \frac{m}{\frac{1000}{M_1}}$$

where m is the molality of the solution and M_1 is the molecular weight of the solvent, equation 6 becomes

$$\Delta T_b = \frac{RT^2 M_1}{1000\Delta H_{\text{vap.}}} m \tag{7}$$

or

$$\Delta T_b = K_b m \tag{8}$$

where K_b is a constant characteristic of the solvent defined by the equation:

$$K_b = \frac{RT^2 M_1}{1000\Delta H_{\text{vap.}}} \tag{9}$$

These relations show that in dilute solution the elevation of the boiling point is proportional to the concentration of the solute, and this direct proportionality has been abundantly verified by experiment.

K_b is called the molal elevation of the boiling point. However, it must be emphasized that this molal boiling-point constant is not the

actual elevation for a 1-molal solution, for in such a concentrated solution the assumptions made in deriving equation 8 would not be valid. Rather, K_b is the limit of $\Delta T_b/m$, that is, the boiling-point elevation per mole, as the concentration becomes zero. It may be evaluated theoretically, from the thermodynamic quantities in equation 9 or experimentally, by measurement of the rise in boiling point produced by a small known concentration of a solute whose molecular weight is known. The values of K_b obtained thermodynamically agree closely with those obtained experimentally.

Example 2. Find the molal boiling-point constant for water, which boils at 100° with the absorption of 539.7 cal per gram.

$$K_b = \frac{1.987 \times 373.1^2 \times 18.02}{1000 \times (539.7 \times 18.02)} = 0.513$$

In practical problems where w_2 grams of solute having a molecular weight of M_2 is added to w_1 grams of solvent, equation 8 becomes

$$\Delta T_b = K_b m = K_b \frac{w_2}{M_2} \frac{1000}{w_1} \tag{10}$$

Example 3. What is the boiling point of a solution containing 90 g of water and 2.00 g of cane sugar (molecular weight = 342)?

$$\Delta T_b = K_b \frac{w_2}{M_2} \frac{1000}{w_1} = 0.513 \times \frac{2.00}{342} \times \frac{1000}{90.0} = 0.0333$$

$$\text{Boiling point} = 100 + 0.033 = 100.033°$$

Experimental Determination of Boiling Points. The importance of molecular weights in establishing the formulas of new compounds has been discussed in an earlier chapter. Frequently it is impossible to vaporize the material for a vapor-density measurement on account of thermal decomposition. The molecular weight M_2 may then be determined from the elevation of the boiling point ΔT_b which is produced by dissolving the material in a suitable solvent. Calculations are made with the help of equation 10. The molal boiling-point constants for several solvents are given on page 237.

Experimental methods for the accurate determination of the elevation of the boiling point have been the object of considerable investigation. The temperature of the boiling solution and not that of the vapor is desired. Therefore the thermometer bulb must be placed directly in the liquid. The liquid, however, is likely to become superheated and register a temperature considerably above its true boiling point. This

difficulty has been overcome by heating the solution locally with electrically heated wires immersed in the solution. Small bubbles of vapor are formed which prevent superheating.

In another method the vapor from the boiling liquid pumps a mixture of liquid and vapor into an inverted funnel just below the surface. The mixture then goes upward in a tube which discharges the mixture onto the thermometer bulb, placed above the liquid. During the passage of the vapor and liquid through this tube the two have opportunity to come to equilibrium, and any superheated liquid is cooled by further evaporation to the normal boiling point.

In carrying out these determinations of the boiling points of solutions, a weighed quantity of solute is introduced into a weighed quantity of solvent. In a better procedure, however, samples are withdrawn and analyzed by chemical or physical means. Since the boiling point is affected by changes in the atmospheric pressure, the determinations on the solution and solvent must be made simultaneously in two pieces of apparatus, or over such short periods of time that the barometer fluctuations are negligible. In accurate work, a barostat may be used to maintain a fixed pressure for all determinations. By automatic regulation with an electric circuit, compressed air is admitted into a chamber whenever the mercury monometer falls below a predetermined pressure. The need of these precautions is evident from the fact that a change of 0.3 or 0.4 mm changes the boiling point of most solvents by 0.01°.

Lowering of the Freezing Point. It has long been known that the freezing point of water, or other liquid, is lowered by the addition of a solute, and it was pointed out by Blagden more than a century ago that the depression of the freezing point is directly proportional to the concentration of the solution. The reason for the lowering may be understood with the help of **Fig. 63.** At the freezing point the solid and the liquid are in equilibrium and both must have the same vapor pressure. If the solid has a greater pressure than the liquid, it will distil over into the liquid phase; if the liquid has the greater pressure, it will change into the solid. When solid and liquid solvent are in equilibrium, and a solute is dissolved in the liquid, the solid solvent will disappear if the temperature is maintained constant, but the disappearance of the solid may be stopped and a state of equilibrium established by lowering the temperature. It may be remembered that the vapor-pressure–temperature curve of a solid is steeper than that of the corresponding liquid because the heat of sublimation of the solid is greater than the heat of vaporization of the liquid. At the intersection of the two curves, solid and liquid are in equilibrium, and the corre-

sponding temperature is the freezing point. The greater the concentration of the solution, the lower is the vapor-pressure curve and the lower is the freezing point of the solution, that is, the temperature at which the vapor curve of the solution intersects the vapor curve of the ice.

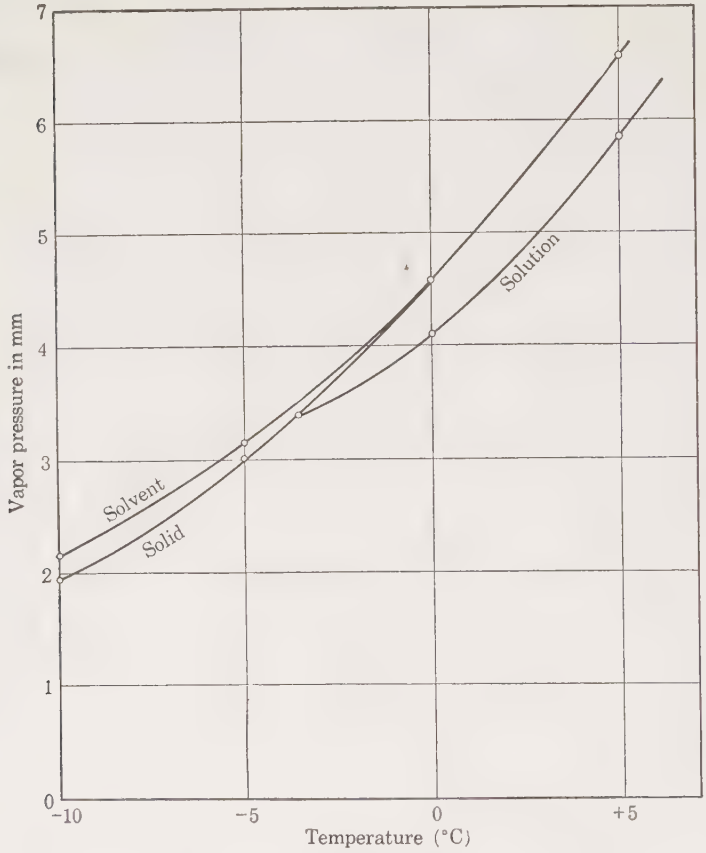


FIG. 63. Lowering of the freezing point of a solvent by a solute—a 2.56 molal solution of sodium chloride in water.

The quantitative relation between the concentration of the solution and the freezing-point depression can be derived as follows:

Let p_s be the vapor pressure of the pure solid solvent (ice in the case of water), let p be the vapor pressure of the solution, and let p^0 be the vapor pressure of the pure solvent in the liquid state. The derivation is limited to solutions in which the solvent freezes out as a pure solid unmixed with the solute. (Most solutions, including aqueous ones, freeze in this manner, but in some cases a solid solution is formed, as

described on page 326.) By Raoult's law, which holds in dilute solutions,

$$p = p^0 N_1$$

where N_1 is the mole fraction of the solvent. At the freezing point of the solution, a state of equilibrium exists, and

$$p_s = p = p^0 N_1$$

Then, differentiating with respect to temperature, we have

$$\frac{dp_s}{dT} = N_1 \frac{dp^0}{dT} + p^0 \frac{dN_1}{dT} \tag{11}$$

Substituting for dp_s/dT and dp^0/dT in equation 11 their equivalents in terms of the molar heat of sublimation of the solid solvent $\Delta H_{\text{sub.}}$ and the molar heat of vaporization of the liquid solvent $\Delta H_{\text{vap.}}$, as given by the Clausius–Clapeyron equation, we have

$$\frac{dp_s}{dT} = \frac{\Delta H_{\text{sub.}} p_s}{RT^2} \quad \text{and} \quad \frac{dp^0}{dT} = \frac{\Delta H_{\text{vap.}} p^0}{RT^2}$$

$$\frac{\Delta H_{\text{sub.}} p_s}{RT^2} = N_1 \frac{\Delta H_{\text{vap.}} p^0}{RT^2} + p^0 \frac{dN_1}{dT} \tag{12}$$

Remembering that $p_s = p^0 N_1$, canceling out equivalent terms, and rearranging, we have

$$\frac{\Delta H_{\text{sub.}} - \Delta H_{\text{vap.}}}{RT^2} = \frac{d \ln N_1}{dT} \tag{13}$$

The molar heat of fusion $\Delta H_{\text{fus.}}$ is equal to the difference between the molar heat of sublimation and the molar heat of vaporization. Then,

$$\frac{\Delta H_{\text{fus.}}}{RT^2} = \frac{d \ln N_1}{dT} \tag{14}$$

Integrating between the limits, T corresponding to the freezing point of the solution, and T_0 corresponding to the freezing point of the pure solvent where $N_1 = 1$, yields

$$\frac{\Delta H_{\text{fus.}}}{R} \int_T^{T_0} \frac{dT}{T^2} = \int_{N_1}^{1} d \ln N_1$$

and

$$\frac{\Delta H_{\text{fus.}}(T_0 - T)}{RT_0 T} = -\ln N_1 \tag{15}$$

This is an exact equation for solutions which obey Raoult's law, provided that the heat of fusion $\Delta H_{\text{fus.}}$ is constant between T_0 and T and that the vapor obeys the simple gas law.

In a binary solution which contains only one solute and one solvent, the mole fraction of the solvent N_1 is equal to $1 - N_2$, where N_2 is the mole fraction of the solute. In dilute solutions a simplification may be made. Expanding by MacLaurin's series gives

$$-\ln N_1 = -\ln (1 - N_2) = N_2 + \tfrac{1}{2}N_2^2 + \tfrac{1}{3}N_2^3 + \cdots \qquad (16)$$

and, remembering that for small values of N_2 the higher powers may be neglected as an approximation in comparison with the first power,* we find

$$-\ln N_1 = -\ln (1 - N_2) \cong N_2$$

and, substituting into equation 15,

$$N_2 = \frac{\Delta H_{\text{fus.}}(T_0 - T)}{RT_0T} \qquad (17)$$

If the freezing-point depression $T_0 - T$ is designated by ΔT_f and it is remembered that, since N_2 is small, T_0 and T are nearly the same, equation 17 may be written in an approximate form as

$$\Delta T_f = \frac{RT_0^2}{\Delta H_{\text{fus.}}} N_2 = \frac{RT_0^2}{\Delta H_{\text{fus.}}} \frac{n_2}{n_1 + n_2} \qquad (18)$$

Equation 18 is like equation 5, except that it applies to the freezing point instead of to the boiling point. It can be shown in a manner similar to that employed in the case of equation 5 that

$$\Delta T_f = K_f m \qquad (19)$$

and that

$$K_f = \frac{RT_0^2}{\Delta H_{\text{fus.}} \times \dfrac{1000}{M_1}} \qquad (20)$$

where K_f is the freezing-point constant or molal lowering. According to these relations, in dilute solutions the lowering of the freezing point is directly proportional to the molality m_2 of the solute, and it is clear why the simple proportionality fails in the more concentrated solutions.

Experimental facts are in agreement with this formula.

* For example, if $N_2 = 0.01$, the expression becomes $0.01 + \frac{1}{2}(0.0001) + \frac{1}{3}(0.000001)$, which is equal to 0.01 within one half of one per cent.

Example 4. For water K_f has the value 1.86°, calculated as follows:

$$K_f = \frac{RT_0^2M_1}{\Delta H_{\text{fus.}} \times 1000} = \frac{1.987 \times 273.1^2 \times 18.02}{(18.02 \times 79.7) \times (1000)} = 1.860$$

According to this equation a normal solute added to 1000 g of water will lower the freezing point at the rate of 1.86° per mole, but the relation holds only for dilute solutions. Even a 1-molal solution is too concentrated, and the depression will be something less than 1.86°. In very concentrated solutions the behavior may become quite complex.

The molecular weight can be determined from the freezing-point depression by use of the following formula, similar to equation 10,

$$\Delta T_f = K_f \frac{w_2}{M_2} \frac{1000}{w_1} \tag{21}$$

The freezing-point constant like the boiling-point constant may be evaluated by direct experiment with a solute of known molecular weight.

The freezing-point constants and boiling-point constants are given in Table I for a number of different solvents.

TABLE I

MOLAL FREEZING-POINT AND BOILING-POINT CONSTANTS

Solvent	Freezing Point	K_f	Boiling Point	K_b
Acetic acid	17	3.9	118.1	2.93
Acetone	....	.....	56.0	1.71
Benzene	5.4	5.12	80.2	2.53
Chloroform	....	.....	60.2	3.63
Ethanol	....	.....	78.3	1.22
Ethylene bromide	10	12.5	.....	....
Ethyl ether	....	.....	34.4	2.02
Heptachloropropane	29.5	12.0	.....	....
Naphthalene	80	6.8	.....	....
Tribomophenol	95	20.4	.....	....
Water	0	1.860	100	0.51

Equation 15 may be written in the form

$$\ln N_1 = \frac{\Delta H_{\text{fus.}}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \tag{22}$$

where T_0 is the freezing point of the solvent, T the freezing point of the solution, and N_1 the mole fraction of the solvent. As such, it finds application in the study of solutions. When $\log N_1$ is plotted against $1/T$, a straight line is produced if the heat of fusion is independent of temperature, if the solution is ideal, and if the solid separates as a pure component.

Experimental Determination of Freezing Points. Freezing-point depressions can be determined with great accuracy. Measurements of moderate accuracy may be made easily with simple apparatus. The freezing points of the pure solvent and the solution are determined with an accurate thermometer. A tube containing the solution is jacketed and immersed in a bath of ice and salt. It is provided with a stopper through which an efficient ring stirrer, encircling the thermometer, is operated with a vertical movement. The temperature gradually falls until the solid appears, and the first steady temperature is recorded as the freezing point. The concentration of the solution in equilibrium with the solid solvent is determined by analyzing the solution.

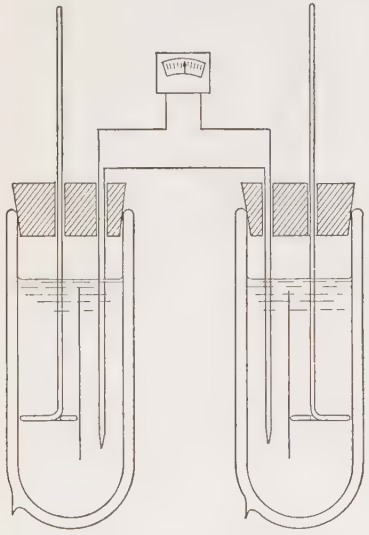


FIG. 64. Apparatus for measuring the freezing-point lowering by a solute.

In a less accurate method, the solution is made up to a known concentration by direct weighing of the solute and solvent, but, if much of the solvent freezes out, the concentration will be different at the time the thermometer reading is taken. This difficulty is accentuated by supercooling which leads to the freezing out of a considerable quantity of solvent.

The most accurate results are obtained with two vacuum-jacketed vessels placed in an ice bath and partly filled with cracked ice, as shown in **Fig. 64.** One vessel contains solvent; the other solution. The difference in temperature is measured to one ten thousandth of a degree with a multiple-junction thermoelement and sensitive potentiometer. The two liquids are stirred vigorously, and the concentration of the solution in equilibrium with the ice is determined accurately by chemical analysis or by physical measurements, for example, with a refractometer.

Table II gives a series of results on aqueous solutions of mannitol measured in this way. The close agreement between observed depressions and the depression as calculated by equation 20 lends proof to the validity of the freezing-point laws.

TABLE II

Lowering of Freezing Point of Water by Mannitol[1]

Moles per 1000 g H_2O	ΔT_f (obs)	ΔT_f (calc)
0.00402	0.0075	0.0075
0.00842	0.0157	0.0156
0.01404	0.0260	0.0261
0.02829	0.0525	0.0525
0.06259	0.1162	0.1162

[1] Adams, *J. Am. Chem. Soc.*, **37**, 481 (1915).

Osmosis. Closely related to the lowering of the freezing point and the lowering of the vapor pressure is the phenomenon of osmosis, that is, the passage of a solvent through a membrane from a dilute solution into a more concentrated one. This phenomenon was first observed in 1748 by Abbé Nollet. If sufficient pressure is applied to the more concentrated solution (by means of a piston, a column of mercury, or a column of the solution) the passage of solvent will reverse its direction. The extra pressure which must be applied to the solution in order to prevent the osmotic flow of pure solvent into the solution is known as the *osmotic pressure* of the solution.

Many theories have been proposed to explain the passage of solvent through a semipermeable membrane from a dilute solution to a more concentrated one. The semipermeable membrane is a barrier so constituted that the solvent can pass through the membrane, but the dissolved material cannot pass. From a thermodynamic standpoint the solvent merely moves from a region where its escaping tendency is large (its vapor pressure is high) to a region where its escaping tendency is small. The presence of the dissolved material lowers the escaping tendency of the solvent, and the greater the concentration, the greater is the lowering.

A simple illustration is offered by putting a dish containing pure water and one containing a solution of sugar or other material into an empty desiccator, and immersing it in a thermostat. After standing,

the level of the solution will rise, and that of the pure water will fall, owing to the diffusion of the water vapor from the pure solvent, where the vapor pressure is high, to the solution, where the vapor pressure is relatively low.

One of the ways in which a semipermeable membrane may function is shown schematically in **Fig. 65.** Very small passages exist in the semipermeable membrane, so small that the liquids are kept from flowing through by surface tension, even if a large hydrostatic pressure is applied. But the solvent molecules can still pass through in the vapor phase as individual molecules, and there will be a steady migration from the solvent to the solution as indicated by the arrows representing vapor pressures—the heavier arrow indicating the higher vapor pressure of the solvent. The solute cannot pass through by this mechanism since it is nonvolatile. That this mechanism is possible has been proved by the osmosis which occurs when a solution is separated from a solvent by a glass tube containing many infinitesimal cracks.

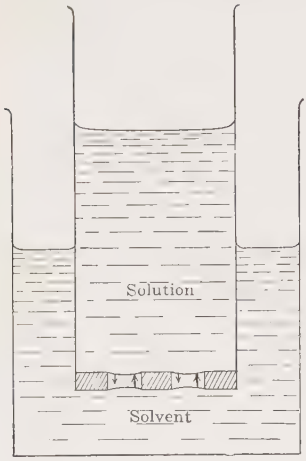


FIG. 65. Hypothetical semipermeable membrane with exaggerated pores showing passage of solvent in gaseous state.

Many semipermeable membranes are more complex than these systems of minute passages which permit the diffusion of gases but do not permit the diffusion of liquids. Animal membranes and certain gelatinous materials offer a medium for the diffusion of water but not for the diffusion of the solute. Solubility of the solvent in the membrane provides another way in which a semipermeable membrane may operate. For example, if a rubber membrane separates a solution of sugar in pyridine from pure pyridine, the pyridine dissolves in the rubber and passes through it from the solvent into the solution.

Ostwald demonstrated theoretically that the pressure due to osmosis must be independent of the nature of the membrane employed in measuring it. Thus, in **Fig. 66,** A and B represent two different semipermeable membranes in an imaginary apparatus. If the nature of the membrane has any influence on the osmotic pressure, the osmotic pressure P_B may be imagined greater than the osmotic pressure P_A. Under this condition the flow in the compartment between the membranes will be to the left from B to A, and the solvent may be returned to the right through a turbine which may be made to do mechanical

work. After being returned to the compartment at the right, it will flow into the solution and, thence, through the cycle repeatedly. But such an arrangement would be a means of producing energy at constant temperature in a cyclic process. Since such perpetual motion is contrary to experience, the premise of two different membranes must be wrong, and it is concluded that all semipermeable membranes give the same osmotic pressure.

In actual practice different membranes may appear to give different hydrostatic pressures, but, if sufficient time is allowed for the attainment of equilibrium, and if the membrane does not leak, the pressures

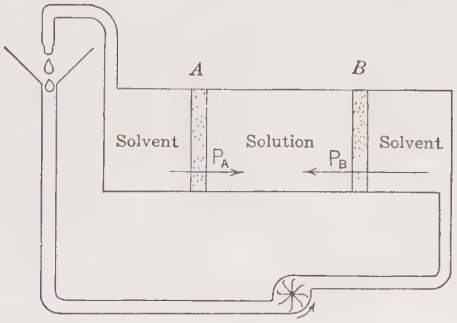


FIG. 66. Hypothetical experiment proving that the osmotic pressure is not affected by the nature of the semipermeable membrane.

ultimately will be the same. The nature of the membrane and its area determine how *rapidly* osmosis occurs but not the osmotic pressure at equilibrium. If any solute diffuses through the membrane, the membrane is not truly semipermeable. Examples of dialysis where certain solutes diffuse through and others do not are discussed later (page 527).

Osmotic Pressure. The first direct measurements of osmotic pressure were made by the botanist, Pfeffer, in 1877. Using a mercury manometer he was able to measure the hydrostatic pressure generated in a solution by the osmotic flow of water through a semipermeable membrane into a solution of sugar. Pfeffer's results are given in Tables III and IV. The approximate volume of solution holding 1 g of cane sugar is given under v, the osmotic pressure in atmospheres under P, and the absolute temperature under T.

The significance of Pfeffer's measurements was first perceived by van't Hoff,* who pointed out the existence of a striking parallelism between the properties of gases and the osmotic properties of solutions. As shown in Table III, the product Pv is a constant, just as it is for

* Van't Hoff, *Z. physik Chem.*, **1**, 481 (1887).

gases according to Boyle's law. As shown in Table IV, the pressure is proportional to the absolute temperature just as it is for gases; that is, P/T = constant.

TABLE III

Relation of Osmotic Pressure to Concentration at 287° K

v (ml)	P (atm)	Pv
100	0.70	70
50	1.34	67
25	2.74	68
16.5	4.10	68

TABLE IV

Relation of Osmotic Pressure to Temperature

Approximately 1 g per 100 ml of solution

T (°K)	P (atm)	P/T
273.0	0.649	0.00238
279.8	0.664	0.00237
286.7	0.691	0.00241
288.5	0.684	0.00237
295.0	0.721	0.00244
305.0	0.716	0.00235
309.0	0.746	0.00241

Moreover, the two relations may be combined to give the same constant R as is obtained for gases,

$$Pv = nRT = \frac{g}{M}RT \tag{23}$$

where P is osmotic pressure, v is the volume of the solution, and g is the weight of solute having molecular weight M.

Example 5. From Pfeffer's data in Table IV, it is seen that 1 g in 100 ml or 1 mole (342 g) in 34.2 liters gives an osmotic pressure of 0.649 atm at 0°.

Then,

$$R = \frac{Pv}{T} = \frac{0.649 \times 34.2}{273} = 0.0813 \text{ liter-atm per degree}$$

Within the limits of the experimental error, this is the same as the gas constant R, namely, 0.08205, and the standard equation used for making calculations on gases can thus be used for calculating approximate osmotic pressures.

Example 6. If 2.00 g of sugar having a molecular weight of 342 is dissolved in 50 ml of solution at 25°, what will be the osmotic pressure?

$$P = \frac{g}{M}\frac{RT}{v} = \frac{2.00 \times 0.08205 \times 298.1}{342 \times 0.0500} = 2.86$$

In concentrated solutions equation 23 fails to give accurate results just as the simple gas laws fail to apply when the gases are placed under high pressure. One correction which helps considerably in the case of gases is the subtraction from the total volume of a term to allow for the volume of the molecules themselves, designated in the case of gases by the term b in van der Waals' equation. A similar correction helps also in calculating the osmotic pressure of concentrated solutions. Thus Berkeley and Hartley * measured the osmotic pressure of sugar solutions at 0° and found, for example, that in a solution containing 660.5 g of sugar per liter (nearly 2-molar) the experimentally determined osmotic pressure at 0° was 100.8 atm, and the value calculated by equation 23 was 51.2 atm. However, if the effective volume is taken as the volume of the solution minus the volume of the sugar, the calculated osmotic pressure is about 75 atm. In general, somewhat better results can be obtained in calculating osmotic pressures of concentrated solutions if the volume is taken as the volume of the solvent rather than the volume of the solution. In aqueous solution, this is equivalent to taking the volume as that of the solvent which contains 1 mole, that is, the reciprocal of the molality. In dilute solutions, of course, there is no difference between the volume of the solvent and that of the solution, and equation 23 is then adequate.

The discrepancy between experiment and theory in concentrated solutions is not peculiar to osmotic pressure. Ideal solutions are rare, and we have to accept the fact that the behavior of concentrated solutions is too complicated to be explained by the simple laws which we have thus far developed. Undoubtedly the nature of the solvent itself is affected by the presence of a high concentration of solute.

Osmotic pressure has been measured up to 250 atm, a tube of porous porcelain material being used as the semipermeable membrane, in the pores of which is deposited a precipitate of copper ferrocyanide. The solvent is placed inside the tube which in turn is surrounded by the solution in a gun-metal tube. When solvent passes through this semipermeable membrane, the volume decrease is registered on a capillary

* Berkeley and Hartley, *Trans. Roy. Soc. (London)*, **A 206**, 481 (1906).

tube. Pressure is applied sufficient to prevent this osmotic flow and maintain constant the level of the solvent in the capillary tube. This pressure is the osmotic pressure.

Comparison of Experimental Methods. The four properties of solutions which have just been studied, vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure, are closely connected. The freezing-point depression can be measured most accurately and most easily, whereas the osmotic pressure can be measured least accurately and only with difficulty. The freezing-point method is limited to low temperatures where the solubility is often small. The boiling-point readings may be seriously affected by fluctuations in the barometric pressure, and, in water, the molal elevation is only about one third as great as the freezing-point depression. The temperature range is limited in both the boiling-point and the freezing-point method. The vapor-pressure lowering is adaptable to different temperatures and capable of high accuracy, but it requires more elaborate apparatus. Osmotic pressure was extensively used in the early development of the theory of solutions, and it is important historically, but at present the concept of vapor-pressure lowering is much more useful in the theoretical treatment of solutions.

Free Energy of Dilution. The properties of a system are conveniently and quantitatively defined in terms of energy. In the study of solutions, for example, the free energy of dilution is a useful thermodynamical quantity. The free energy of dilution may be calculated by means of formula 24, which holds true at constant temperature for a system doing no work other than expansion work, as shown on page 152.

$$dF = v\,dp \qquad (24)$$

A large reservoir of solution having a vapor pressure p is placed near a reservoir of pure solvent having a vapor pressure p^0. The temperature T is kept constant throughout. One mole of solvent is vaporized from the solution by keeping the pressure infinitesimally less than p. The quantity of solution is so great that the removal of 1 mole of solvent does not appreciably increase the concentration of the solution. Since the process is carried out reversibly at constant temperature and pressure, the free-energy change for process I is zero.

(I) 1 mole of solvent in solution $\rightarrow$ 1 mole solvent as vapor:

$$\Delta F = 0$$

The mole of vapor is placed in a cylinder provided with a piston and compressed reversibly (that is, by infinitesimal increases of pressure) until its pressure is p^0. This process may be written as process II.

(II) 1 mole of solvent as vapor at pressure $p \rightarrow 1$ mole of solvent as vapor at pressure p^0:

$$F^0 - F = \Delta F = \int_p^{p^0} V\,dp = \int_p^{p^0} \frac{RT}{p}\,dp = RT \ln \frac{p^0}{p}$$

where F^0 is the free energy of 1 mole of the vapor at pressure p^0, and F is the free energy at pressure p.

This mole of solvent vapor is then added reversibly to the reservoir of pure solvent by applying an external pressure infinitesimally greater than p^0. The process may be written as process III.

(III) 1 mole solvent as vapor at vapor pressure $p^0 \rightarrow 1$ mole solvent as liquid:

$$\Delta F = 0$$

All the steps are carried out isothermally and reversibly, and the total change of free energy involved in the transfer of 1 mole of solvent from solution to solvent is

$$\Delta F = RT \ln \frac{p^0}{p} \tag{25}$$

This value of ΔF for the transfer is applicable, regardless of how the transfer is carried out.

This formula can be used equally well for transferring a mole of solvent from a solution of one concentration c_1 having a vapor pressure p_1 to a solution of another concentration c_2 having a vapor pressure p_2. Thus,

$$\Delta F = RT \ln \frac{p_2}{p_1} \tag{26}$$

Moreover, these formulas are not limited to the solvent. They may be applied to any volatile material in the solution whether called solvent or solute.

In ideal solutions where the vapor pressure of the volatile component is proportional to the mole fraction N, the equation is written thus:

$$\Delta F = RT \ln \frac{N_2}{N_1} \tag{27}$$

In very dilute solutions where Raoult's law applies or in any ideal solutions, the vapor pressures are proportional to the concentration of the solute; thus,

$$\Delta F = RT \ln \frac{c_2}{c_1} \tag{28}$$

Example 7. What is the free energy of dilution involved when 1 mole of a volatile solute in a 0.01 molal aqueous solution at 25° is mixed with enough water to give a 0.001 molal solution?

$$\Delta F = RT \ln \frac{c'}{c} = 1.987 \times 298.1 \times 2.303 \times \log \frac{0.001}{0.01} = -1364 \text{ cal}$$

The negative sign indicates that the process of dilution is spontaneous. The reverse process in which the solute becomes more concentrated would not occur spontaneously as explained on page 157. ΔF would have a positive sign.

It has been shown that the four properties, vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure, may be readily calculated for dilute solutions, but that the simple formulas fail when applied to concentrated solutions. It is a necessary consequence of thermodynamics, however, that at a given temperature the deviations from ideal solutions are the same in all the different properties. For example, if the vapor-pressure lowering is known, the osmotic pressure may be calculated with exactness, even in concentrated solutions where Raoult's law does not hold and where the osmotic pressure cannot be calculated from the gas laws. These relations follow from the fact that the free energy of dilution is the same, no matter whether it is effected by evaporation, by freezing, or by application of pressure through a semipermeable membrane.

The free energy of transfer of a mole of solvent from solution to solvent is given by equation 25. The transfer of solvent may be effected also by osmosis. A large quantity of the solution is placed in a cylinder provided with a movable semipermeable membrane for a piston, and the pressure is slowly increased from atmospheric pressure to $P + 1$, where P is the osmotic pressure. The free-energy change for this step is obtained by integration of equation 24; if the liquid is incompressible, we have

$$\Delta F = \int_1^{P+1} v_1 \, dP = v_1 P$$

where v_1 is the volume of the solution.

Then the pressure is increased infinitesimally, and solvent passes through the semipermeable membrane, because extra pressure on the solution is slightly greater than the osmotic pressure P. The free-energy change in this step is zero since this is an isothermal reversible process in which the pressure on each phase is kept constant.

After 1 mole of solvent has been forced out,* it is taken from the

* It is assumed here that the molecular weight is the same in the liquid and gaseous states. If it is not, sufficient liquid is removed to produce 1 mole of vapor.

cylinder, and the pressure on the remaining volume of solution v_2 is slowly reduced to 1 atm.

$$\Delta F = -v_2 P$$

The total change in free energy is

$$\Delta F = (v_1 - v_2)P = V'P \tag{29}$$

where V' or $(v_1 - v_2)$ is the partial molal volume of the solvent. It is very nearly equal to the volume of 1 mole of the pure solvent and may be taken as such in most calculations.

Combining equations 25 and 29 yields

$$PV' = RT \ln \frac{p^0}{p}$$

$$P = \frac{RT}{V'} \ln \frac{p^0}{p} \tag{30}$$

With this formula it is possible to calculate the osmotic pressure of a solution, from the vapor pressures of the solvent and the solution, and the molar volume of the solvent. At high concentrations, where the osmotic pressures calculated by the simple gas law (equation 23) are in error by more than 30 per cent, the values calculated by equation 30 check with the observed values within less than 1 per cent.

Example 8. Calculate the osmotic pressure of a 1M sucrose solution in water from the fact that at 30° the vapor pressure of the solution is 31.207 mm. The vapor pressure of water at 30° is 31.824 mm. The density of pure water is 0.99564.

$$P = \frac{RT}{V'} \ln \frac{p^0}{p}$$

$$V' = \frac{18.02}{0.99564} = 18.10 \text{ ml} \quad \text{or} \quad 0.0181 \text{ l}$$

$$P = \frac{0.08205 \times 2.303}{0.0181} \left(\log \frac{31.824}{31.207} \right) \times 303.1$$

$$= 26.93 \text{ atm}$$

Equation 30 can be used also for deriving formula 23. For ideal solutions or dilute solutions, where Raoult's law holds,

$$p = p^0 N_1$$

where N_1 is the mole fraction of the solvent. Then,

$$\ln \frac{p^0}{p} = -\ln N_1 \tag{31}$$

Since N_1 is equal to $1 - N_2$, where N_2 is the mole fraction of the solute,

$$\ln N_1 = \ln (1 - N_2) \tag{32}$$

Then substituting into equation 30 gives

$$P = \frac{RT}{V'}[-\ln (1 - N_2)] \tag{33}$$

Expanding in a series, we have

$$P = \frac{RT}{V'}\left(N_2 + \frac{1}{2}N_2^2 + \frac{1}{3}N_2^3 + \cdots\right) \tag{34}$$

When N_2 is small, higher powers may be neglected, and

$$PV' = N_2RT \tag{35}$$

But $N_2 = n_2/(n_1 + n_2)$, and in dilute solutions $N_2 = n_2/n_1$, where n_2 is the number of moles of solute and n_1 the number of moles of solvent. Therefore,

$$PV'n_1 = n_2RT \tag{36}$$

Setting v, the volume of the dilute solution containing n_2 moles of solute equal to the volume of the solvent, $V'n_1$ (that is, to the volume of 1 mole of solvent $\times$ the number of moles of solvent) gives

$$Pv = n_2RT \tag{37}$$

This is equivalent to equation 23, discovered experimentally, and it is evident from the approximations introduced why it cannot hold for concentrated solutions.

Dissociation of Solutes. If the nonvolatile solute is broken down into smaller nonvolatile units in solution, the effect on the vapor pressure and other related properties will be increased. Van't Hoff pointed out that dilute aqueous solutions of most inorganic acids, bases, and salts give abnormally large osmotic pressures, whereas dilute solutions of sugar and many organic substances give osmotic pressures in close agreement with the values calculated with the simple law $PV = RT$. He found that by introducing an additional term i he could obtain agreement with experimental values using the formula:

$$PV = iRT \tag{38}$$

At first i was regarded as a constant, but it was soon found that it decreases as concentration of the solute increases. The value of i may be

determined for any solution by comparing the osmotic pressure or any of the related properties of the solution with these properties as measured for a normal solute such as sucrose. Thus

$$i = \frac{P}{P_0} = \frac{\Delta p}{(\Delta p)_0} = \frac{\Delta T_f}{(\Delta T_f)_0} = \frac{\Delta T_b}{(\Delta T_b)_0} \tag{39}$$

where the subscript zero refers to the solution of a normal solute. The vapor-pressure lowering Δp is equal to $p_{\text{solvent}} - p_{\text{solution}}$.

The abnormal behavior of salts is easily observed in the depression of the freezing points of solutions. Since for a normal solute $\frac{\Delta T_f}{m}$ is 1.86, $i = \frac{\Delta T_f}{m} \Big/ 1.86$. Usually the molal freezing point depressions $\Delta T_f/m$ are considerably greater than 1.86.

The data are shown graphically in **Fig. 67** where it is seen that i approaches the values 2, 3, and 4 at infinite dilution. It is evident that the

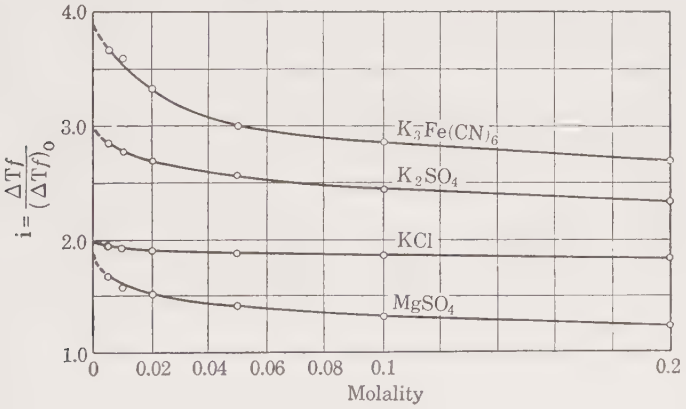


FIG. 67. Values of i extrapolated to infinite dilution for electrolytes of different valence types.

depressions are considerably greater than those of normal solutes such as sucrose or mannitol. For a given solute they increase as the concentration is decreased and, at infinite dilution, approach definite limits which are multiples of the normal depression 1.86°. Thus, with solutions of KCl and $MgSO_4$, the molal depression approaches the value 3.72° (or $2 \times 1.86°$) as the solutions are diluted, while the respective limits toward which the molal depressions of solutions of K_2SO_4 and $K_3Fe(CN)_6$ tend are $3 \times 1.86°$ and $4 \times 1.86°$.

These facts, together with numerous other properties of dilute solu-

tions of acids, bases, and salts, find their most satisfactory explanation in the theory of electrolytic dissociation.

Arrhenius' Theory of Electrolytic Dissociation. In 1887 Arrhenius * proposed the theory that aqueous solutions of acids, bases, and salts are dissociated, to a greater or less extent, into positively and negatively charged particles or *ions*, and that the increase in the number of dissolved units due to this dissociation is the cause of the enhanced osmotic pressure. These ions, like the original solutes from which they come, are nonvolatile. Arrhenius strengthened this theory greatly by pointing out that substances which give abnormal osmotic effects yield solutions which conduct the electric current, whereas solutions of such substances as cane sugar, urea, and alcohol, which exert normal osmotic pressures, do not conduct electricity any better than the pure solvent. In other words, only electrolytes † are capable of undergoing ionic dissociation, and exhibiting abnormally large osmotic pressures and related effects; hence Arrhenius termed the hypothesis the *electrolytic dissociation theory*. When electrically charged electrodes are introduced into the solution, the positive ions move toward the negative electrode, and the negative ions move toward the positive electrode, the passage of a current through the solution consisting in the transfer of electric charges. The relation between electrical conductance and the degree of ionization is discussed on page 483.

The chemical properties of an ion are very different from the properties of the corresponding atom or molecule. For example, sodium ions are stable in an aqueous solution of sodium chloride, whereas sodium atoms in the electrically neutral condition react violently with water, evolving hydrogen and forming a solution of sodium hydroxide. Chlorine in such compounds as $CHCl_3$, CCl_4, is not precipitated by silver nitrate, since these compounds are not dissociated by water.

Arrhenius pointed out further that the multiples of the normal freezing-point depression at infinite dilution, such as are shown in Fig. 67, are identical with the number of ions into which a molecule of solute can dissociate. Thus KCl can dissociate into two ions, K^+ and Cl^-, and at infinite dilution the depression is just twice the normal value. In other words, i is 2. For K_2SO_4 three ions are possible, $2K^+$ and $SO_4^=$; thus i has a value of 3 at infinite dilution. Likewise $MgSO_4$ gives two ions, and $K_3Fe(CN)_6$ gives four ions, $3K^+$ and $Fe(CN)_6^{\equiv}$. This explanation of Arrhenius has been abundantly verified.

* Arrhenius, *Z. physik Chem.*, **1**, 631 (1887).

† The term *electrolyte* strictly refers to the solution of an ionized substance, although it is often applied to acids, bases, or salts, because, when dissolved, they produce electrolytes.

Example 9. The freezing point of a 0.01 molal solution of barium chloride is $-0.050°$. What is the approximate vapor pressure of the solution at 25° if the vapor pressure of pure water is 23.756 mm?

$$i = \frac{\Delta T_f}{(\Delta T_f)_0} = \frac{0.050}{0.01 \times 1.86} = 2.7$$

$$\Delta p = i \frac{n_2 p^0}{n_1} = 2.7 \frac{0.01}{\frac{1000}{18.02}} 23.756 = 0.0115$$

$$p = 23.756 - 0.0115 = 23.744 \text{ mm}$$

Further discussion of the constant i and the influence of concentration on the behavior of electrolytes is deferred until page 508.

REFERENCES

Hildebrand, "Solubility," Reinhold Publishing Corp., New York, 1936.

Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, 1946, Chapter IX.

Swietoslawski, "Ebulliometry," Jagellonian University Press, Krakow, 1936.

PROBLEMS

1. The vapor pressure of a solution containing 13 g of solute in 100 g of H_2O at 28° is 27.371 mm. Calculate the molecular weight of the solute. The vapor pressure of water at this temperature is 28.065 mm. *Ans.* 92.3.

2. Purified nitrogen gas is slowly bubbled through a solution of 3.000 g of a nonvolatile organic compound dissolved in 200 g of benzene and then bubbled through pure benzene. The solution is found to be 2.1540 g lighter, while the pure benzene suffered a loss in weight of 0.0160 g. What is the apparent molecular weight of the dissolved substance? *Ans.* 157.

3. If 68.4 g of sugar (molecular weight = 342) is dissolved in 1000 g of water, what are (*a*) the vapor pressure, and (*b*) the osmotic pressure, at 20°? (*c*) What is the freezing point? (*d*) What is the boiling point? The density of the solution at 20° is 1.024. The vapor pressure of water at 20° is 17.363. The heat of vaporization of water is 539 cal per gram, and the heat of fusion is 79.6 cal per gram.

Ans. (*a*) 17.30 mm. (*b*) 4.61 atm. (*c*) $-0.372°$. (*d*) 100.103°.

4. Ten grams of benzene, 10 g of toluene, and 10 g of naphthalene are added together to give a homogenous solution. If it is assumed that the solution is ideal, how many grams of toluene will be vaporized by passing through 10 liters of air at 30° if the vapor pressure of toluene at this temperature is 36.7 mm, that of benzene is 118.5 mm, and that of naphthalene is negligible? *Ans.* 0.617 g.

5. Solutions of hydrogen chloride in chlorobenzene obey Henry's law. In dilute solutions,

$$K = \frac{p}{m} = 0.438$$

where p is given in atmospheres and m is molality. What is the partial pressure of

HCl in mm of hydrochloric acid over a 1 per cent by weight solution of HCl in chlorobenzene? *Ans.* 93.2 mm.

6. An aqueous solution of maltose at 25° has a vapor pressure of 23.476 mm whereas pure water has a vapor pressure of 23.756 mm. What is the osmotic pressure of the solution? *Ans.* 16.11 atm.

7. When cells of the skeletal muscle of a frog were placed in a series of sodium chloride solutions of different concentrations, it was observed microscopically that the cells remained unchanged in 0.7 per cent NaCl solution but shrank in more concentrated solutions and swelled in more dilute solutions. Calculate the osmotic pressure of the cell protoplasm at 25°. *Ans.* 5.91 atm.

8. Show that the free energy of mixing of two liquids which form a perfect solution is

$$\Delta F = n_2 RT \ln N_2 + n_1 RT \ln N_1$$

9. Calculate ΔF for the mixing of 1 mole of benzene and 1 mole of toluene, to give an ideal solution at 25°. *Ans.* −822 cal.

10. Given a 0.01 molal solution of urea in water at 25°, calculate (*a*) the boiling point of the solution.

(*b*) The vapor pressure of the solution if the vapor pressure of pure water is 23.756.

(*c*) The osmotic pressure (assuming that the density of the solution is practically 1.0).

11. On the basis of Raoult's law and the relation that the vapor pressure of the solvent in solution is proportional to the mole fraction of the solvent, show that $\Delta p/p = n_2/n_1$.

12. Calculate the vapor pressure of a 15 per cent solution of urea NH_2CONH_2 at 25°. The vapor pressure of water at this temperature is 23.756.

13. (*a*) If 10 g of phenol added to a given quantity of benzene lowers the freezing point of benzene X°, how many degrees (in terms of X) will 20 g lower it if the solutions are ideal?

(*b*) The boiling point of a certain solvent is B°, and the boiling point of a solution of this solvent containing 10 per cent by weight of a nonvolatile solute is $B + Y$°. Calculate in terms of B and Y the boiling point of a solution containing 20 per cent by weight of the solute, assuming an ideal solution.

14. Calculate the freezing-point depression of water produced by dissolved air in equilibrium with air (79 per cent nitrogen, 21 per cent oxygen) at 1 atm. At 0°, 100 g of water dissolves 4.49 ml of oxygen and 2.35 ml of nitrogen when the pressure of each gas is 1 atm.

15. Calculate the melting point of a solution of 20 g of naphthalene $C_{10}H_8$ in 80 g of heptachloropropane, C_3HCl_7.

16. When 1.4511 g of dichloroacetic acid is dissolved in 56.8699 g of carbon tetrachloride, the boiling point is increased 0.518°. The boiling point of carbon tetrachloride is 76.75°, and its heat of vaporization is 46.5 cal per gram at the boiling point. What is the molecular weight of the acid? How can the discrepancy be explained?

17. Calculate the change in free energy involved when a mole of water is transferred (by isothermal distillation) at 25° from pure water to a large quantity of a 9.9 per cent glycerol solution which has a vapor pressure of water amounting to 23.300 mm. The vapor pressure of pure water is 23.756 mm.

18. Human blood freezes at −0.56°. (*a*) What is its osmotic pressure at 37°? (*b*) What is the free-energy change when one mole of water is evaporated from this blood?

19. A certain number of grams of a given substance in 100 g of benzene lowers the freezing point by 1.28°. The same weight of solute in 100 g of water gives a freezing point of −1.395. If the substance has its normal molecular weight in benzene and is completely dissociated in water, into how many ions does a molecule of this substance dissociate when placed in water?

---

20. The vapor pressure of water at 25° is 23.756 mm. Calculate the vapor pressure of solutions containing (*a*) 6.01 g of urea NH_2CONH_2, (*b*) 0.94 g of phenol C_6H_5OH, and (*c*) 6.01 g of urea + 9.4 g of phenol per 1000 g of water, assuming no chemical action between the two substances. (*d*) Calculate (*c*) assuming that a stable compound is formed containing 1 mole of the urea to 1 mole of phenol.

21. Using in part data from an earlier chapter, calculate the boiling point of a solution containing 10 g of heptachloropropane in 100 g of carbon tetrachloride, assuming that the heptachloropropane is nonvolatile.

22. (*a*) How many grams of methanol CH_3OH must be added to a 10-liter tank of water to prevent freezing at −5°? (*b*) How many grams of calcium chloride $CaCl_2$, assuming complete dissociation and no interaction? (*c*) How many grams of glycol $(CH_2OH)_2$?

23. Derive an equation which relates the elevation in the boiling point of a liquid by the addition of a nonvolatile solute to the corresponding lowering of the vapor pressure.

24. Ten grams of benzene vaporizes isothermally from a solution containing an equimolecular mixture of benzene and diphenyl and condenses in a large amount of solution of benzene and nitrobenzene in which the mole fraction of benzene is 0.1. Calculate the change in free energy at 25°, assuming that both solutions are ideal.

25. (*a*) What molal concentration of solutes at 20° is required to raise by osmosis a column of solution having a density of approximately 1.0 to a height of 100 ft? *

(*b*) What is the vapor pressure of the solution at 20°? The vapor pressure of pure water at 20° is 17.363.

26. The total vapor pressure of a solution containing 3 per cent by weight of ethanol C_2H_5OH in water is 760 mm at 97.11°. The vapor pressure of pure water at this temperature is 685 mm. Using Raoult's law and Henry's law, calculate the partial pressure at 97.11° of ethanol and water over a solution containing 0.02 mole fraction of ethanol.

---

27. By combining Raoult's law, the Clausius–Clapeyron equation, and Trouton's rule, show that the boiling point T_B of a dilute solution of a nonvolatile solute and the mole fraction of *solvent* N_A are related by the approximate equation:

$$N_A T_B^{21/R} = \text{constant}$$

* The rise of the sap in a tall tree is not to be attributed *entirely* to osmosis.

CHAPTER XII

CHEMICAL EQUILIBRIA

The Law of Mass Action. The idea of the reversibility of chemical reactions seems to have been first stated clearly in 1799 by C. Berthollet, while he was acting as scientific adviser to Napoleon in Egypt. He noted the deposits of sodium carbonate in certain salt lakes and concluded that they were produced by the high concentration of sodium chloride and dissolved calcium carbonate, the reverse of the laboratory experiment in which sodium carbonate reacts with calcium chloride to precipitate calcium carbonate.

In 1862 the influence which the concentration of alcohol and acetic acid have on the amount of ethyl acetate formed was reported by M. Berthelot and St. Gilles.

These investigations and others led Guldberg and Waage to state the *mass law* according to which *the rate of a chemical reaction is proportional to the active masses of the reacting materials.* They realized clearly that the important factor is not the quantity of reactants but the quantity of reacting material *per unit of volume.* They defined active mass as the molecular concentration. The mass law has come to be the foundation of much of our quantitative formulation of rates of chemical reaction and chemical equilibria. If we use concentrations in moles per liter in our modern formulas, the results are not exact, but, if we use *activities* which are defined arbitrarily, our calculations are accurate.

In general, a reversible reaction may be written

$$A + B + \cdots \rightleftharpoons G + H + \cdots \tag{1}$$

and the concentrations c of each constituent in moles per liter may be written c_A, c_B, c_G, c_H. According to the mass law, the speed with which A and B react depends on the concentrations of A and B. Then,

$$\text{Rate}_{\text{forward reaction}} \propto c_A c_B \quad \text{or} \quad \text{Rate}_{\text{forward reaction}} = k_1 c_A c_B$$

where k_1 is the specific rate constant. The rate is greatest when A and B are first mixed together, and it gradually decreases as these reactants are used up.

The products of the reaction, G and H can react in the reverse reac-

tion to give A and B, and the rate of this reaction also depends on the concentration of G and H. Then,

$$\text{Rate}_{\text{reverse reaction}} = k_2 c_G c_H$$

When more than 1 mole of a single substance is involved in the equation of a reaction, the number of moles must be considered in the mass law because the reaction rate depends on the number of collisions. Thus, if the reaction involves $2A + 1B$, the collisions of 1 mole of A with a second mole of A will be as frequent as with a mole of B and so the rate expression will be $k_1 c_A c_A c_B$ or

$$\text{Rate} = k_1 {c_A}^2 c_B$$

In the more general equation, each of the substances in the equation has a coefficient, 1, 2, or 3, etc., and equation 1 may be rewritten

$$aA + bB + \cdots \rightleftharpoons gG + hH + \cdots \tag{2}$$

showing that a moles of A and b moles of B react to give g moles of G and h moles of H. At equilibrium,

$$\text{Rate}_{\text{forward reaction}} = \text{Rate}_{\text{reverse reaction}}$$

$$k_1 {c_A}^a {c_B}^b \cdots = k_2 {c_G}^g {c_H}^h \cdots$$

and

$$\frac{{c_G}^g {c_H}^h \cdots}{{c_A}^a {c_B}^b \cdots} = \frac{k_1}{k_2} = K_c \tag{3}$$

where K_c is a constant defined as the equilibrium constant expressed in concentrations. Concentrations are usually given in moles per liter. A more rigorous derivation for the equilibrium constant is given by means of thermodynamics on page 269. It can be shown that equations 3 and 4 are strictly true only for ideal dilute solutions and ideal gases.

Equilibrium Constants. In the study of equilibria in solutions K_c is widely used, but in various equilibria the concentration of the gases is frequently given in terms of the partial pressures p of the gases. Since, at any one temperature, the partial pressure p of an ideal gas is proportional to its concentration c in the gas phase, we may write equation 3 in the following manner:

$$K_p = \frac{{p_G}^g {p_H}^h \cdots}{{p_A}^a {p_B}^b \cdots} \tag{4}$$

where K_p is the equilibrium constant expressed in partial pressures. Unless otherwise specified, the pressures are given in atmospheres.

The values of K_c can be easily converted into K_p because $c = 1/v = p/RT$ where c is expressed in moles per liter or in the reciprocal of the number of liters containing one mole, and p is expressed in atmospheres. Substituting these values of c into equation 3, we have

$$K_c = \frac{\left(\frac{p_G}{RT}\right)^g \left(\frac{p_H}{RT}\right)^h}{\left(\frac{p_A}{RT}\right)^a \left(\frac{p_B}{RT}\right)^b} = \left(\frac{1}{RT}\right)^{(g+h)-(a+b)} \frac{{p_G}^g \times {p_H}^h}{{p_A}^a \times {p_B}^b} = (RT)^{(a+b)-(g+h)} K_p \tag{5}$$

Letting Δn equal the change in the number of moles of gas during the reaction, that is $(g + h) - (a + b)$, we have

$$K_p = K_c(RT)^{\Delta n} \tag{6}$$

In reactions where the same number of moles of gas occur on both sides of the equation, $\Delta n = 0$ and $K_c = K_p$. Since concentrations are expressed in moles per liter and partial pressures in atmospheres, it is evident that the gas constant R must be expressed in liter-atmospheres.

Example 1. For the reaction $N_2 + 3H_2 = 2NH_3$, at 400°:

$$K_c = \frac{{c_{NH_3}}^2}{c_{N_2} \times {c_{H_2}}^3} = 0.507$$

Calculate K_p.

$$K_p = (RT)^{\Delta n} K_c = (0.08205 \times 673.1)^{-2} \times 0.507 = 1.66 \times 10^{-4}$$

A large value of K_p means that the numerator is greater than the denominator, and a small value means that it is smaller. In this reaction the ammonia concentration at equilibrium is high when K_p is large, and it is low when K_p is small. The magnitude of the equilibrium constant is a measure of the extent to which the materials react to give the products, that is, a measure of chemical affinity.

Certain conventions are observed in the use of equilibrium constants to avoid confusion. *The equation for the reaction is always given*, and *the products at the right of the equality sign are placed in the numerator.*

When the equation for the reaction is reversed, the new equilibrium constant becomes the reciprocal of the other. Thus rewriting Example 1,

$$2NH_3 = N_2 + 3H_2$$

$$K_c = \frac{c_{N_2} \times {c_{H_2}}^3}{{c_{NH_3}}^2} = \frac{1}{0.507} = 1.97$$

If the reaction is written

$$NH_3 = \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2$$

$$K_c = \frac{\sqrt{c_{N_2}}\sqrt{c_{H_2}^{\,3}}}{c_{NH_3}} = \sqrt{1.97} = 1.40$$

These fractional exponents are usually avoided by multiplying through by an appropriate integer.

Determination of Equilibrium Constants. Many chemical and physical measurements can be used in the determination of equilibrium constants. A considerable amount of ingenuity is often needed, not only in devising methods for analyzing the mixture without disturbing the equilibrium but also in calculating the concentration of all the substances present from an experimental determination of only one or two.

If there is a change in pressure or in volume during the reaction, the composition at equilibrium can be calculated readily, as shown in the following section. Other physical properties, such as absorption of light, or refractive index or electrical conductance, can be used in special cases to determine the concentration of one or more of the substances at equilibrium. Frequently chemical methods can be used, but, if they involve a different temperature, it is necessary to "freeze" the equilibrium mixture in some way so that it will not shift during the analysis. Sudden chilling or addition of an excess of some chemical reagent or removal of a catalyst is often effective for this purpose.

Usually the original concentrations of the reactants are known, and their concentrations at equilibrium are determined directly, or they are calculated indirectly from the concentration of the products of equilibrium. For example, in the reaction,

$$A + B \rightleftharpoons G + H$$

if 1 mole of A and 1 mole of B are mixed in a volume of 1 liter and allowed to come to equilibrium, and if 0.9 mole per liter of G is found by analysis, it follows that the concentration of H must equal that of G, and the concentration of A and of B at equilibrium must be $1 - 0.9$ or 0.1. The equilibrium constant then is written

$$K_c = \frac{c_G \times c_H}{c_A \times c_B} = \frac{0.9 \times 0.9}{0.1 \times 0.1} = 81$$

It is essential to know that equilibrium has been reached before the analysis of the mixture can be safely used for calculating the equilibrium constant. Sometimes the reaction is very slow and the mixture may be far from equilibrium even though it does not appear to change. The following may serve as criteria for the attainment of equilibrium.

1. The same equilibrium constant is obtained when the equilibrium is approached from both sides. In the example given, the same value is obtained for K when A and B are mixed as when G and H are mixed.

2. The same equilibrium constant is obtained when the concentrations of reacting materials are varied over a wide range.

3. When the mixture is allowed to stand for longer and longer periods, a concentration is finally reached which does not change with further standing.

Flow methods are sometimes used for determining equilibrium constants. For example, known mixtures of nitrogen and hydrogen are forced through a heated chamber (containing a catalyst), and the issuing gas is passed quickly through a capillary tube to an absorption bottle where the ammonia is titrated. The partial pressures of all three gases can then be calculated. The gas is passed through at various rates of flow, and the equilibrium constant is calculated when the passage through is so slow that making it still slower does not increase the concentration of ammonia. When equilibrium is established, a longer period of time will not produce any further change in the concentrations.

Dissociation of Gases. The determination of the density of a gas provides one of the simplest methods for measuring quantitatively the extent to which the gas is dissociated. When a gas dissociates, more molecules are produced, and at constant temperature and pressure the volume increases. The density or the weight per liter then decreases, and the difference between the density of the undissociated gas and the partially dissociated gas permits a calculation of the degree of dissociation.

If we start with 1 mole of gas and let α represent the fraction dissociated, then $1 - \alpha$ will denote the fraction remaining undissociated. If 1 mole of gas yields ν moles of gaseous products, the total number of moles present at any time will be

$$(1 - \alpha) + \nu\alpha \quad \text{or} \quad 1 + (\nu - 1)\alpha$$

Since the density of a given weight of gas at constant pressure is *inversely* proportional to the number of moles, the ratio of the density

d_1 of the undissociated gas to the density of the partially dissociated gas d_2 is given by the expression,

$$\frac{d_1}{d_2} = \frac{1 + (\nu - 1)\alpha}{1} \tag{7}$$

$$\alpha = \frac{\frac{d_1}{d_2} - 1}{\nu - 1} = \frac{d_1 - d_2}{d_2(\nu - 1)} \tag{8}$$

It is always advantageous to visualize a formula if possible by checking it with some simple calculation. With reference to equation 8, if there is no dissociation $\alpha = 0$ and $d_1 = d_2$; if dissociation is complete, $\alpha = 1$ and $d_2(\nu - 1) = d_1 - d_2$ or $d_1 = \nu d_2$. Obviously, both these relations are in agreement with the experimental facts.

Molecular weights may be substituted for densities, giving

$$\alpha = \frac{M_1 - M_2}{M_2(\nu - 1)} \tag{9}$$

where M_1 is the molecular weight of the undissociated gas and M_2 is the average molecular weight of the gases when the gas is partly dissociated. Densities are converted into molecular weights by multiplying the molar volume in liters at a given temperature by the weight of 1 liter. The use of formula 9 is illustrated in Table I with the reaction,

$$N_2O_4 \rightleftharpoons 2NO_2$$

in which $\nu = 2$.

TABLE I

DENSITIES OF PARTIALLY DISSOCIATED NITROGEN TETROXIDE (N_2O_4) AT ONE ATMOSPHERE PRESSURE

Temp., °C	Average Molecular Weight Partially Dissociated Gas (M_2)	$\alpha = \frac{92.02 - M_2}{M_2}$
15	82.00	0.122
25	77.64	0.185
35	72.45	0.270
45	66.80	0.378
55	61.24	0.502
65	56.51	0.628
75	52.85	0.741

The mean molecular weight M_2 of the partially dissociated gas is determined experimentally, and M_1 is taken as the theoretical molecular weight of undissociated nitrogen tetroxide (N_2O_4), that is, 92.02. Here there is a simple quantitative check on the dissociation process, for the NO_2 formed by dissociation is brown, and the undissociated N_2O_4 is colorless. It is easily noticed that the color becomes darker brown as the temperature is raised and the density becomes less. The intensity of the brown color may be measured quantitatively with a colorimeter or photoelectric colorimeter.

Example 2. If 1.588 g of nitrogen tetroxide gives a total pressure of 760 mm when partially dissociated in a 500-cc glass vessel at 25°, what is the degree of dissociation α?

$$Pv = \frac{g}{M} RT$$

$$M_2 = \frac{RT}{P}\frac{g}{v} = \frac{0.08205 \times 298.1 \times 1.588}{1 \times 0.500}$$

$$= 77.68$$

$$\alpha = \frac{92.02 - 77.68}{77.68} = 0.1846$$

Equilibrium Constants in Gases. The dissociation of nitrogen tetroxide is represented by the equation,

$$N_2O_4 \rightleftharpoons 2NO_2$$

and

$$K_p = \frac{p_{NO_2}{}^2}{p_{N_2O_4}} \tag{10}$$

If α represents the degree of dissociation, $(1 - \alpha)$ is proportional to the number of moles of undissociated N_2O_4; 2α is proportional to the number of moles of NO_2; and $(1 - \alpha) + 2\alpha$ or $1 + \alpha$ is proportional to the total number of moles.

If the total pressure is P, the partial pressures are as follows:

$$p_{N_2O_4} = \frac{1 - \alpha}{1 + \alpha} P \quad \text{and} \quad p_{NO_2} = \frac{2\alpha}{1 + \alpha} P$$

Then,

$$K_p = \frac{\left(\frac{2\alpha}{1 + \alpha} P\right)^2}{\frac{1 - \alpha}{1 + \alpha} P} = \frac{4\alpha^2 P}{1 - \alpha^2} \tag{11}$$

In this reaction there is an increase in volume, 1 mole of gas dissociating into 2. According to the principle of Le Chatelier, it is possible to predict qualitatively that a decrease of pressure will cause the system to shift toward $2NO_2$, which occupies the larger volume. Equation 11 makes it possible to calculate quantitatively the degree of dissociation of N_2O_4 at any pressure.

Example 3. At 25.0° and 1 atm, nitrogen tetroxide has been found by vapor density measurements to be 18.46 per cent dissociated. Find K_p.

$$K_p = \frac{4\alpha^2 P}{1 - \alpha^2} = \frac{4 \times (0.1846)^2}{1 - (0.1846)^2} \times 1 = 0.141$$

Calculate the degree of dissociation of nitrogen tetroxide at 0.5 atm and 25°.

$$K_p = 0.141 = \frac{4\alpha^2(0.5)}{1 - \alpha^2}$$

and

$$0.141(1 - \alpha^2) = 2\alpha^2$$

$$\alpha = 0.257$$

Another gaseous equilibrium only slightly more complicated than the dissociation of nitrogen tetroxide is the dissociation of phosphorous pentachloride. At temperatures something over 200° C the following reaction takes place:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

When 1 mole of PCl_5 dissociates, there will be at equilibrium $1 - \alpha$ mole of PCl_5, α mole of PCl_3, and α mole of Cl_2, where α is the degree of dissociation. If these gases are contained at equilibrium in a vessel of v liters, the concentrations in moles per liter are

$$c_{PCl_5} = \frac{1 - \alpha}{v}; \quad c_{PCl_3} = \frac{\alpha}{v}; \quad \text{and} \quad c_{Cl_2} = \frac{\alpha}{v}$$

The total number of moles is

$$[1 - \alpha] + \alpha + \alpha = 1 + \alpha$$

and the mole fractions are

$$N_{PCl_5} = \frac{1 - \alpha}{1 + \alpha}; \quad N_{PCl_3} = \frac{\alpha}{1 + \alpha}; \quad \text{and} \quad N_{Cl_2} = \frac{\alpha}{1 + \alpha}$$

If P is the total pressure, the partial pressures are

$$p_{PCl_5} = \frac{1 - \alpha}{1 + \alpha} P; \quad p_{PCl_3} = \frac{\alpha}{1 + \alpha} P; \quad \text{and} \quad p_{Cl_2} = \frac{\alpha}{1 + \alpha} P$$

The equilibrium constant can be expressed in moles per liter (K_c), or in partial pressures (K_p), as follows:

$$K_c = \frac{c_{PCl_3} \times c_{Cl_2}}{c_{PCl_5}} = \frac{\frac{\alpha}{v} \times \frac{\alpha}{v}}{\frac{1-\alpha}{v}} = \frac{\alpha^2}{(1-\alpha)v} \tag{12}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\frac{\alpha}{1+\alpha}P \times \frac{\alpha}{1+\alpha}P}{\frac{1-\alpha}{1+\alpha}P} = \frac{\alpha^2}{1-\alpha^2}P \tag{13}$$

Several examples will be given to illustrate the calculation and use of equilibrium constants.

Example 4. At 250° 1 liter of partially dissociated phosphorus pentachloride gas, at 1 atm, weighs 2.695 g. Calculate the degree of dissociation α from the measured density of the gas and calculate the equilibrium constant K_p. If we start with 1 mole of phosphorus pentachloride having a molecular weight M of 208.3, there are $1 + \alpha$ moles in the partially dissociated gas, and the density d is given by the expression:

$$d = \frac{g}{v} = \frac{M}{1+\alpha} \times \frac{P}{RT} \tag{14}$$

$$d = 2.695 = \frac{208.3 \times 1}{(1+\alpha)0.08205 \times 523.1}$$

$$\alpha = 0.80$$

According to equation 13,

$$K_p = \frac{0.80^2 \times 1}{1 - 0.80^2} = 1.78$$

This reaction is an interesting one to study in more detail. Qualitatively, it can be seen that increasing the total pressure will decrease the amount of dissociation, because the undissociated gas occupies the smaller volume. If chlorine is added, p_{Cl_2} increases, and, since K_p remains constant, p_{PCl_3} must diminish, and p_{PCl_5} must increase. The degree of dissociation is decreased also by the addition of p_{PCl_3}. In general the dissociation of any substance is repressed by the addition of its dissociation products. The addition of an inert gas at constant volume has no effect on the dissociation as long as the partial pressures of the gases remain unchanged.

Example 5. What will be the degree of dissociation of phosphorus pentachloride when 0.1 mole at 250° is placed in a 3-liter vessel containing chlorine at 0.5 atm pressure? Let x = the additional number of moles of chlorine or phosphorus trichloride formed by the dissociation of the phosphorus pentachloride.

$$K_p = 1.78 = \frac{p_{PCl_3}p_{Cl_2}}{p_{PCl_5}} = \frac{\frac{xRT}{v}\left(0.5 + \frac{xRT}{v}\right)}{\frac{(0.1 - x)RT}{v}} = \frac{x\left[0.5 + \frac{(0.08205)(523.1)x}{3}\right]}{0.1 - x}$$

$$x = 0.0574$$

The degree of dissociation = 0.0574/0.1 = 0.574.

Example 6. How many moles of PCl_5 must be added to a liter vessel at 250° in order to obtain a concentration of 0.1 mole of chlorine per liter?

x = number of moles of PCl_5 added to vessel

$$K_p = 1.78 = \frac{p_{PCl_3}p_{Cl_2}}{p_{PCl_5}} = \frac{\left(0.1\,\frac{RT}{v}\right)\left(0.1\,\frac{RT}{v}\right)}{(x - 0.1)\,\frac{RT}{v}} = \frac{0.1^2}{(x - 0.1)} \times \frac{RT}{v}$$

$$= \frac{0.01 \times 0.08205 \times 523.1}{(x - 0.1)}$$

$$x = 0.341 \text{ mole}$$

Examples 5 and 6 could have been worked out just as well by converting K_p into K_c and then making the calculations with K_c in moles per liter.

Example 7. Under what total pressure must an equimolecular mixture of chlorine and phosphorus trichloride be placed in order to obtain 1 atm of phosphorus pentachloride at 250°? If we let $x = p_{PCl_3} = p_{Cl_2}$ at equilibrium,

$$K_p = \frac{p_{PCl_3}p_{Cl_2}}{p_{PCl_5}} = \frac{x^2}{1}$$

$$x = 1.33 \text{ atm}$$

The total pressure at equilibrium is

$$p_{PCl_3} + p_{Cl_2} + p_{PCl_5} = 1.33 + 1.33 + 1 = 3.66 \text{ atm}$$

Example 8. Under what pressure must an equimolecular mixture of chlorine and phosphorus trichloride be placed at 250° in order to obtain an 80 per cent conversion of the phosphorus trichloride into phosphorus pentachloride?

$$K_p = 1.78 = \frac{\alpha^2}{1 - \alpha^2}P = \frac{0.20 \times 0.20}{1 - 0.20^2}P$$

$$P = 42.7 \text{ atm}$$

Another classical example of an equilibrium in gases is the dissociation of hydrogen iodide or hydriodic acid gas at temperatures above 400°.

Very careful measurements are available * for the equilibrium

$$2HI \rightleftharpoons H_2 + I_2$$

Quartz vessels of known volume were filled with hydriodic acid at a measured pressure and heated in an electric thermostat to 425.1° for several hours until equilibrium was established. The vessels were then chilled quickly and analyzed for iodine by titration with sodium thiosulfate. The concentration of hydrogen at equilibrium is equal to that of the iodine. The concentration of hydriodic acid at equilibrium is obtained by subtracting the iodine from the initial hydriodic acid. The equilibrium concentrations in moles per liter are shown in Table II.

TABLE II

Equilibrium between Hydrogen, Iodine and Hydriodic Acid at 698.6 K

c_{I_2} (mole/liter) $\times 10^3$	c_{H_2} (mole/liter) $\times 10^3$	c_{HI} (mole/liter) $\times 10^3$	$K = \frac{c_{H_2}c_{I_2}}{c_{HI}^2}$
1.7069	2.9070	16.482	1.827×10^{-2}
1.2500	3.5600	15.588	1.831
0.7378	4.5647	13.544	1.835
2.3360	2.2523	16.850	1.853
3.1292	1.8313	17.671	1.835
0.4789	0.4789	3.531	1.840
1.1409	1.1409	8.410	1.840
0.4953	0.4953	3.655	1.832

The last three sets of data were obtained by starting from the other side of the equilibrium, weighing the initial quantity of iodine, measuring the pressure of hydrogen, and titrating the iodine after reaching equilibrium. The hydriodic acid concentration was determined by subtracting the final iodine concentration from the initial concentration. The close check between the two sets of data show that equilibrium was reached in every case.

Sometimes calculations are facilitated by expressing the concentrations with letters. Thus, if a moles of hydrogen is mixed with b moles of iodine, and $2x$ moles of hydriodic acid is formed, when equilibrium

* Taylor and Crist, *J. Am. Chem. Soc.*, **63**, 1381 (1941).

is established, $a - x$ is the amount of hydrogen, and $b - x$ is the amount of iodine present. Then, substituting these quantities into the expression for the equilibrium constant gives

$$K_c = \frac{c_{H_2} c_{I_2}}{c_{HI}^2} = \frac{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}{\left(\frac{2x}{v}\right)^2} = \frac{(a-x)(b-x)}{4x^2} \tag{15}$$

$$x = \frac{a + b - \sqrt{(a-b)^2 + 16abK_c}}{2(1 - 4K_c)} \tag{16}$$

It is of interest to note that a change in pressure does not alter the equilibrium in this gaseous reaction. Making use of the partial pressures of the components of the gaseous system, instead of the concentrations, we have

$$\frac{p_{H_2} \times p_{I_2}}{p_{HI}^2} = K_p$$

Now, if the total pressure on the system is increased to n times its original value, all the partial pressures are increased in the same proportion, and

$$\frac{np_{H_2} \times np_{I_2}}{n^2 p_{HI}^2} = K_p$$

which is seen to be equivalent to the original expression, since n cancels out. The equilibrium is thus seen to be independent of the pressure. This independence applies only to those systems in which no change in volume occurs during the reaction. It may be remembered also that in this case $K_p = K_c$.

Illustrations of the calculations of more complicated gaseous equilibria will now be given.

Example 9. The reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$ was investigated by passing mixtures of CO_2 and H_2 over a catalyst at 900° at 1 atm pressure. The resulting gas was chilled quickly to room temperature by passage through a capillary and was analyzed. In one experiment the partial pressures were as follows: $CO_2 = 0.2142$; $H_2 = 0.2549$; $CO = 0.2654$; $H_2O = 0.2654$ atm. Calculate the number of moles of hydrogen present in another equilibrium mixture containing 22.72 moles of CO, 22.72 moles of H_2O, and 48.50 moles of CO_2.

$$K_p = \frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}} = \frac{0.2654 \times 0.2654}{0.2142 \times 0.2549} = 1.290$$

$$K_p = 1.290 = \frac{\left(22.72\frac{RT}{v}\right)\left(22.72\frac{RT}{v}\right)}{\left(48.50\frac{RT}{v}\right)\left(x\frac{RT}{v}\right)}$$

$$x = \frac{22.72^2}{48.50 \times 1.290} = 8.25 \text{ moles } H_2$$

Example 10. Ammonia is formed from a mixture of three parts of hydrogen and one part of nitrogen (page 385). At lower temperatures the yield is still higher, but the time required for equilibrium to be reached would be too great to be practical, except for the addition of a catalyst. The pressure is kept as high (200 atm) as practical and the temperature as low as practical.

Under equilibrium conditions at 400° and 10 atm pressure 3.85 per cent of ammonia is obtained.

Calculate K_p for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$. The ratio of three volumes of H_2 to one volume of nitrogen is maintained, regardless of the amount of ammonia formed. Of the 96.15 per cent by volume which is not ammonia one fourth is nitrogen and three fourths is hydrogen.

$$K_p = \frac{p_{NH_3}^2}{p_{N_2}p_{H_2}^3} = \frac{(0.0385 \times 10)^2}{(\frac{1}{4} \times 0.9615 \times 10)(\frac{3}{4} \times 0.9615 \times 10)^3} = 0.000164$$

Calculate the total pressure P necessary to give a mixture containing 5 per cent ammonia at this temperature.

$$p_{NH_3} = 0.05P \qquad p_{N_2} = \tfrac{1}{4} \times 0.95P \qquad p_{H_2} = \tfrac{3}{4} \times 0.95P$$

$$K_p = 0.000164 = \frac{(0.05P)^2}{(0.2375P)(0.7125P)^3} = \frac{0.0025P^2}{0.0859P^4}$$

$$P^2 = \frac{0.0025}{0.000164 \times 0.0859} = 177.5 \qquad P = 13.3 \text{ atm}$$

Calculate the percentage of ammonia when the mixture is subjected to a pressure of 50 atm.

$$p_{H_2} = 3p_{N_2} \qquad p_{N_2} + p_{H_2} + p_{NH_3} = 50 \text{ atm} \qquad p_{NH_3} = 50 - 4p_{N_2}$$

$$K_p = 0.000164 = \frac{p_{NH_3}^2}{p_{N_2}p_{H_2}^3} = \frac{(50 - 4p_{N_2})^2}{(p_{N_2})(3p_{N_2})^3} = \frac{(50 - 4p_{N_2})^2}{27p_{N_2}^4}$$

$$\frac{50 - 4p_{N_2}}{p_{N_2}^2} = \sqrt{0.000164 \times 27} = 6.65 \times 10^{-2}$$

$$p_{N_2} = 10.62 \qquad p_{H_2} = 3 \times 10.62 = 31.86$$

$$p_{NH_3} = 50 - (10.62 + 31.86) = 7.52$$

$$\text{Per cent ammonia} = \frac{7.52}{50.0} \times 100 = 15$$

Equilibria in Solutions. Concentrations in solution are frequently expressed in moles per liter. The following reaction is a classical example of an equilibrium involving liquids:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

The volume of the solution is v liters, and the number of moles of each of the four compounds is designated as a, b, c, and d, respectively. The additional number of moles of ester and water formed by the reaction of acetic acid and alcohol is denoted by x. Then, if the slight change in volume of the liquids due to the chemical reaction is neglected, the concentration of each of the compounds is

$$c_{C_2H_5OH} = \frac{a - x}{v}; \qquad c_{CH_3COOH} = \frac{b - x}{v}$$

$$c_{CH_3COOC_2H_5} = \frac{c + x}{v}; \qquad c_{H_2O} = \frac{d + x}{v}$$

Then

$$K_c = \frac{c_{CH_3COOC_2H_5}c_{H_2O}}{c_{CH_3COOH}c_{C_2H_5OH}} = \frac{(c + x)(d + x)}{(a - x)(b - x)} \qquad (17)$$

The use of this equation is illustrated in the following example.

Example 11. One mole of acetic acid is mixed with one mole of ethanol at 25°, and after equilibrium is reached a titration with standard alkali solution shows that 0.667 mole of acetic acid has reacted. Calculate K_c.

$$K_c = \frac{c_{CH_3COOC_2H_5}c_{H_2O}}{c_{CH_3COOH}c_{C_2H_5OH}} = \frac{0.667/v \times 0.667/v}{(1.000 - 0.667)/v \times (1.000 - 0.667)/v} = 4.00$$

When 0.50 mole of ethanol is added to 1.000 mole of acetic acid at 25°, how much ester will be formed at equilibrium?

$$K_c = 4.00 = \frac{x^2}{(1.000 - x)(0.500 - x)}$$

In a quadratic equation two solutions are always possible, but usually one may be shown to be imaginary or incompatible with the physical-chemical facts. In the present case it is impossible to produce more moles of ester than corresponds to the number of moles of ethanol, and so the value 1.577 is ruled out. Actually 0.422 mole of ester and 0.422 mole of water are formed, and (0.500 − 0.422) or 0.078 mole of ethanol and (1.000 − 0.422) or 0.578 mole of acetic acid remain unreacted. An experimental value of 0.414 mole of ester was obtained. Additional calculations are as follows:

Moles ethanol added to 1 mole of acetic acid	0.08	0.28	2.24	8.00
Moles of ethyl acetate calculated	0.078	0.232	0.864	0.945
Moles of ethyl acetate formed experimentally	0.078	0.226	0.876	0.966

It may be noted from this example that a large excess of one of the reactants causes the other reactant to undergo nearly complete reaction.

In the equilibrium just studied, the volume terms cancel out, and so the equilibrium constant is not affected by changing the volume. When there is a change in the number of molecules, however, it is necessary to consider the volume of the solution in calculating the equilibrium constant.

Free-Energy Changes in Chemical Reactions. A very important relation exists between the equilibrium constant and the change in free energy. It connects chemical reactivity with the measurements of thermodynamics and electrochemistry.

The following general reaction is representative of any chemical reaction.

$$aA + bB + \cdots \rightleftharpoons gG + hH + \cdots \tag{18}$$

We will assume at first that A, B, G, and H are ideal gases, each exerting its own partial pressure p_A, p_B, etc. The gases are present in such large quantities that the loss or gain of one mole of a or b does not materially affect the concentrations nor the partial pressures.

It will be remembered from page 152 that

$$\left(\frac{dF}{dp}\right)_T = v = \frac{nRT}{p} \tag{19}$$

Then,

$$F = nRT \ln p + \text{constant} \tag{20}$$

where the integration constant varies with the temperature but is constant at a given temperature.

In the reaction given by equation 18, a moles of the substance A disappear, and the system, therefore, undergoes a loss in free energy of

$$F_A = aRT \ln p_A + C_A$$

Owing to the disappearance of B, the system suffers a further decrease in free energy:

$$F_B = bRT \ln p_B + C_B$$

Owing to the appearance of G and H, the system increases in free energy by the amount,

$$F_G = gRT \ln p_G + C_G$$

and

$$F_H = hRT \ln p_H + C_H$$

The net change in free energy is, therefore,

$$\Delta F = gRT \ln p_G + hRT \ln p_H - aRT \ln p_A - bRT \ln p_B + C \tag{21}$$

where $C = C_G + C_H - C_A - C_B$.

At equilibrium, $\Delta F = 0$; hence

$$\left[\ln \frac{p_G{}^g p_H{}^h}{p_A{}^a p_B{}^b}\right]_{\text{equil.}} = -\frac{C}{RT}$$

This derivation shows that at equilibrium at a given temperature

$$\left[\frac{p_G{}^g p_H{}^h}{p_A{}^a p_B{}^b}\right]_{\text{equil.}} = \text{a constant, } K_p \tag{22}$$

where C is a constant such that $RT \ln K_p = -C$. K_p has been defined previously as an *equilibrium constant.*

If the reactants and products are not at their equilibrium partial pressures p but at any arbitrary pressures p', there is a finite free-energy change, and

$$\Delta F = -RT \ln K_p + RT \ln \frac{p_G{}'^g p_H{}'^h}{p_A{}'^a p_B{}'^b}$$

The quantity $p_G{}'^g p_H{}'^h / p_A{}'^a p_B{}'^b$ is so easily confused with the partial pressures at equilibrium that it is well to rewrite this equation as

$$\Delta F = -RT \ln K_p + RT \ln \frac{p_G{}'^g p_H{}'^h}{p_A{}'^a p_B{}'^b} = -RT \ln K_p + RT \ln Q_p \tag{23}$$

where p refers to the partial pressures at equilibrium, p' refers to non-equilibrium partial pressures of reactants and products, and Q_p is defined as the pressure quotient, $p_G{}'^g p_H{}'^h / p_A{}'^a p_B{}'^b$. This is an exceedingly important equation which will be applied to practical problems in later chapters.

There is a special case which is of importance—that in which the reactants in their standard states (1 atm for gases) react to give the products in their standard states (1 atm). The free-energy change involved in reaction between substances in their standard states is designated with a superscript zero ΔF^0 and is called the standard free-energy change. Under these conditions the last term drops out because all the values of p' are unity, Q is 1 and $\log 1 = 0$, and, then,

$$\Delta F^0 = -RT \ln K_p \tag{24}$$

The superscript zero indicates that the change in free energy refers to *the reaction in which the reactants in their standard states, usually at 1 atm, are converted into products in their standard states (at 1 atm).* This equation shows that the decrease in the standard free energy during a reaction is a measure of the magnitude of the equilibrium constant,

that is, of the chemical affinities involved. It determines just how far the reaction will go and how the partial pressures will be related at equilibrium. Equations 23 and 24 can be combined to give equation 25:

$$\Delta F = \Delta F^0 + RT \ln Q_p \qquad (25)$$

The values of ΔF^0 for many common substances can be found in tables of standard free energies of formation, and equation 25 will then permit one to calculate the free energy change in taking reactants at given partial pressures and converting them into products at given partial pressures.

Example 12. What is ΔF^0 at 25° for the reaction,

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

$$K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}} = 0.141$$

$$\Delta F^0 = -RT \ln K_p = -1.987 \times 298.1 \times 2.303 \log 0.141 = +1161 \text{ cal}$$

According to this calculation, 1 mole of N_2O_4 at 1 atm can be converted into 2 moles of NO_2 at 1 atm and 25°, only with some external aid which is equivalent to a change in free energy of 1161 cal.

Example 13. What is ΔF^0 at 25° for the reaction,

$$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$$

$$K_p = \frac{p_{N_2O_4}}{p_{NO_2}^2} = \frac{1}{0.141} = 7.09$$

$$\Delta F^0 = -RT \ln K_p = -1.987 \times 298.1 \times 2.303 \log 7.09 = -1161 \text{ cal}$$

It is clear that, if a reaction is reversed, the equilibrium constant becomes the reciprocal of that for the forward reaction, and the free-energy change has the same magnitude but the opposite sign.

Example 14. What is the free-energy change involved at 25° if 10 g of N_2O_4 at 2 atm is changed into 10 g of NO_2 at 0 3 atm?

$$\Delta F = -RT \ln K_p + RT \ln Q_p = -RT \ln K_p + RT \ln \frac{p_{NO_2}^2}{p_{N_2O_4}}$$

$$= -1.987 \times 298.1 \times 2.303 \log 0.141 + 1.987 \times 298.1 \times 2.303 \log \frac{0.3^2}{2}$$

$$= 1161 - 1837 = -676 \text{ cal}$$

This free-energy change is for 1 mole of N_2O_4. The free-energy change for 10 g is $(10/92.0) \times (-676) = -73.5$ cal.

Formulas similar to 22–25 may be derived in which the partial pressures are replaced by concentrations. The free-energy change in the

case of dilute ideal solutions, for the isothermal change of state,

$$aA(\text{at } c_A') + bB(\text{at } c_B') \rightleftharpoons gG(\text{at } c_G') + hH(\text{at } c_H')$$

is given by

$$\Delta F = -RT \ln \frac{c_G{}^g c_H{}^h}{c_A{}^a c_B{}^b} + RT \ln \frac{c_G{}'^g c_H{}'^h}{c_A{}'^a c_B{}'^b} = -RT \ln K_c + RT \ln Q_c \quad (26)$$

where the concentrations c_A, c_B, c_G, and c_H are for equilibrium at constant pressure and the concentrations c_A', etc., are arbitrary. If the primed values are all unity, we have again the important equation for the standard free-energy change,

$$\Delta F^0 = -RT \ln K_c \quad (27)$$

In such calculations concentrations are customarily expressed in molalities; the standard state of each solute is taken as the concentration of 1 mole per 1000 g of solvent if the solution is ideal. Molarities expressed in moles per liter are sometimes used. Pressure is fixed, but usually for solutions its value is not important.

Example 15. The equilibrium constant for the association of benzoic acid to a dimer in dilute benzene solutions at 43.9° is 2.7×10^2 in terms of molar concentrations. Calculate ΔF^0, and state its meaning.

$$2C_6H_5COOH = (C_6H_5COOH)_2$$

$$K_c = \frac{c_{\text{dimer}}}{c^2_{\text{monomer}}} = 2.7 \times 10^2$$

$$\Delta F^0 = -RT \ln K_c = -1.987 \times 317.0 \times 2.303 \times 2.4314$$

$$= -3527 \text{ cal}$$

Hence, there is a free-energy decrease of 3527 cal when 2 moles of benzoic acid monomer, C_6H_5COOH, at a concentration of 1 mole per liter of solution, is converted to 1 mole of benzoic acid dimer at a concentration of 1 mole per liter, in benzene at 43.9°. The reaction is spontaneous as written.

In concentrated solutions mole fractions should be used. In ideal concentrated solutions the partial pressures can be calculated accurately from the mole fractions, whereas the calculations based on concentrations may be in serious error. Calculating on the basis of mole fractions gives

$$\Delta F = -RT \ln \frac{N_G{}^g N_H{}^h}{N_A{}^a N_B{}^b} + RT \ln \frac{N_G{}'^g N_H{}'^h}{N_A{}'^a N_B{}'^b} \quad (28)$$

$$= -RT \ln K_N + RT \ln Q_N$$

Example 16. Calculate K_N, assuming ideal solutions, for the following reaction at 25°:

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

if the addition of 1 mole of alcohol to 1 mole of glacial acetic acid yields at equilibrium 0.667 mole of ester. Calculate and interpret ΔF^0.

In this equilibrium mixture,

$$N_{\text{alcohol}} = N_{\text{acid}} = \frac{1.000 - 0.667}{2.000}$$

$$N_{\text{ester}} = N_{\text{water}} = \frac{0.667}{2.000}$$

$$K_N = \frac{\left(\frac{0.667}{2.000}\right)^2}{\left(\frac{0.333}{2.000}\right)^2} = \frac{(0.667)^2}{(0.333)^2} = 4.00$$

$$\Delta F^0 = -RT \ln K_N = -1.987 \times 298.1 \times 2.303 \times \log 4.00$$
$$= -822$$

For this reaction where $\Delta n = 0$, $K_c = K_N = K_p$ and ΔF^0 is the same. When, however, there is a change in the number of molecules, during reaction K_c, K_p and K_N will differ and the ΔF^0s will not be equal. The standard states will then be different.

It is essential to have a clear understanding of the influence of concentration in changing the value and even the sign of ΔF. In the three following examples it is assumed that the solutions are ideal and that equation 26 is exact.

Example 17. In a simple hypothetical reaction such as a change into an isomer,

$$A \rightleftharpoons B$$

if the system is at equilibrium when A and B are at equal concentrations, $a_A = a_B$, what is the value of ΔF^0?

$$K_c = \frac{c_B}{c_A} = 1 \quad \text{and} \quad \Delta F^0 = -RT \ln K_c = -RT \ln 1 = 0$$

Example 18. In another system $C \rightleftharpoons D$ there is a state of equilibrium at 27° when the concentration of the product D is ten times as great as C. What is the value of ΔF^0? In this example and the next few involving ΔF^0 it is assumed that the solutions are ideal

$$K_c = \frac{c_D}{c_C} = \frac{10}{1} \quad \text{and} \quad \Delta F^0 = -RT \ln K_c = -1.987 \times 300.1 \times 2.303 \log 10$$
$$= -1373 \text{ cal}$$

If ΔF^0 has a negative sign, that is, if the free energy of the products is less than the free energy of the reactants, there is a tendency for the reactants (the materials at the left of the reaction as written) at unit concentration to react to give the products at unit concentration.

If a system is in a state of equilibrium when the concentrations of the products are less than those of the reactants, ΔF^0 is positive; there is no tendency for the reactants at unit concentration to react to give the products at unit concentration, but on the contrary the reaction tends to go in the reverse direction.

Example 19. In the reaction $E \rightleftharpoons G$ at 27° there is equilibrium when the concentration of the product is one-tenth that of the reactant E. Calculate ΔF^0.

$$K_c = \frac{c_G}{c_E} = \frac{\frac{1}{10}}{1}, \qquad \Delta F^0 = -RT \ln K_c = -1.987 \times 300.1 \times 2.303 \log \frac{1}{10}$$

$$= -1.987 \times 300.1 \times 2.303 \times (-1) = +1373$$

It is clear from the positive value of ΔF^0 that E at unit concentration will not react spontaneously to give G at unit concentration. However, some production of G can be effected by increasing sufficiently the concentration of E or by reducing the concentration of G by removing it as it is formed at concentrations less than unity.

Example 20. Referring to example 19, calculate ΔF for the reaction at 27° in which E at a concentration of 20 goes to G at a concentration of 1.

$$E(c = 20) \rightleftharpoons G(c = 1)$$

$$\Delta F = -RT \ln K_c + RT \ln \frac{c_G'}{c_E'} = \Delta F^0 + RT \ln \frac{1}{20}$$

$$= 1373 + 1.987 \times 300.1 \times 2.303 \times (-1.301)$$

$$= 1373 - 1786 = -413$$

The negative sign of ΔF in this equation shows that the reaction will take place spontaneously under these conditions. By sufficiently increasing the concentration of E, E can be partially converted into G in spite of the unfavorable equilibrium constant and positive value of ΔF^0. The distinction between ΔF for any concentrations and ΔF^0 for standard states at unit concentration must be kept clearly in mind.

Free-Energy Tables. The change in free energy can be calculated from equilibrium constants for chemical reactions which involve the reactants and products in their standard states. Equation 24 is used more often, however, to calculate equilibrium constants from known values of ΔF^0. If the free-energy change for a given chemical reaction cannot be obtained directly from equilibrium constants, it can often

be calculated indirectly from other reactions for which the free-energy changes are known.

If several reactions are added together, the free-energy changes are additive, just as heats of reaction are additive. The free-energy change of the total reaction is the sum of the free-energy changes of all the composite reactions. Free energies are usually given in calories.

Example 21. Calculate the free energy of formation of hydrochloric acid from its elements at 25° from the following data:

$$H_2O\ (l) = H_2O\ (g) \qquad \Delta F^0 = 2{,}053$$

$$H_2\ (g) + \tfrac{1}{2}O_2\ (g) = H_2O\ (l) \qquad \Delta F^0 = -56{,}560$$

$$H_2O\ (g) + Cl_2\ (g) = 2HCl\ (g) + \tfrac{1}{2}O_2\ (g) \qquad \Delta F^0 = 9{,}123$$

Adding these equations gives

$$H_2\ (g) + Cl_2\ (g) = 2HCl\ (g) \qquad \Delta F^0 = -45{,}384$$

or

$$\tfrac{1}{2}H_2\ (g) + \tfrac{1}{2}Cl_2\ (g) = HCl\ (g) \qquad \Delta F^0 = -22{,}692$$

Just as there are tables of heats of formation (page 129) from which heats of reaction can be calculated, so also are there tables of free energy of formation from which ΔF^0 for various reactions can be calculated. The free energies of the elements at 25° and atmospheric pressure, in their most stable states under these conditions, are taken as zero. The free energy of formation ΔF^0 of a compound is the change in free energy involved when 1 mole of this substance in its standard state at 25° and 1 atm pressure is produced from the elements in their standard states (25° and 1 atm pressure). If the substance is not in its standard state, the superscript zero is omitted. Table III gives a few of these values.

Some of the values of the free energy of formation were obtained directly or indirectly from equilibrium constants; others are obtained from measurements of electromotive force as explained in Chapter XVI, and others are obtained from calorimetric measurements, combining heats of reaction and determinations of absolute entropies as explained on page 286.

The use of this table in calculating free-energy changes may be illustrated with the following example.

Example 22.

$$H_2\ (g) + C_2H_4\ (g) = C_2H_6\ (g)$$

$$\Delta F^0 = \Delta F^0_{\text{products}} - \Delta F^0_{\text{reactants}} = -7787 - (0 + 16{,}279)$$

$$= -24{,}066 \text{ cal (at 25° and 1 atm)}$$

This table gives the changes in free energy for isothermal, isobaric reactions at 25°.

Calculate K_p at 25° for this reaction between hydrogen and ethylene.

$$\Delta F^0 = -24{,}066 = -1.987 \times 298.1 \times 2.303 \log K_p$$

$$K_p = \frac{p_{C_2H_6}}{p_{H_2} \times p_{C_2H_4}} = \text{antilog} \frac{24{,}066}{1.987 \times 298.1 \times 2.303} = 4.39 \times 10^{17}$$

TABLE III

FREE ENERGIES OF FORMATION AT 25° AND 1 ATM [1]

Substance	$\Delta F^0_{298.1K}$	Substance	$\Delta F^0_{298.1K}$
Water, H_2O (*l*)	−56,560	Propylene, C_3H_6 (*g*)	14,730
Water, H_2O (*g*)	−54,507	Acetylene, C_2H_2 (*g*)	50,034
Hydrochloric acid, HCl (*g*)	−22,692	*cis*-2-Butene, C_4H_8 (*g*)	15,570
Hydrobromic acid, HBr (*g*)	−12,540	*trans*-2-Butene, C_4H_8 (*g*)	14,800
Hydriodic acid, HI (*g*)	315	Formaldehyde, CH_2O (*g*)	−26,100
Sulfur, S (rhombic)	0	Formic acid, CH_2O_2 (*g*)	−82,520
Sulfur, S (monoclinic)	18	Formic acid, CH_2O_2 (*l*)	−85,150
Sulfur, S (*g*)	30,240	Methanol, CH_4O (*l*)	−39,960
Hydrogen sulfide, H_2S (*g*)	−7,840	Urea, CH_4N_2O (*s*)	−47,120
Ammonia, NH_3 (*g*)	−3,910	Oxalic acid, $C_2H_2O_4$ (*s*)	−165,900
Nitric oxide, NO (*g*)	20,850	Acetic acid, $C_2H_4O_2$ (*l*)	−94,500
Nitrogen dioxide, NO_2 (*g*)	11,920	Ethyl bromide, C_2H_5Br (*l*)	−6,180
Carbon monoxide, CO (*g*)	−32,700	Ethanol, C_2H_6O (*l*)	−40,200
Carbon dioxide, CO_2 (*g*)	−94,100	Dimethyl ether, C_2H_6O (*g*)	−26,350
Lead oxide, PbO (*s*)	−45,050	Ethylene glycol, $C_2H_6O_2$ (*l*)	−80,200
Silver ion[2], Ag^+	18,448	Acetone, C_3H_6O (*g*)	−36,500
Zinc ion[2], Zn^{++}	−34,984	Acetone, C_3H_6O (*l*)	−37,220
Methane, CH_4 (*g*)	−12,085	Glycerol, $C_3H_8O_3$ (*l*)	−113,600
Ethane, C_2H_6 (*g*)	−7,787	Fumaric acid, $C_4H_4O_4$ (*s*)	−156,700
Propane, C_3H_8 (*g*)	−5,550	Maleic acid, $C_4H_4O_4$ (*s*)	−149,400
n-Butane, C_4H_{10} (*g*)	−3,630	Ethyl acetate, $C_4H_8O_2$ (*l*)	−77,600
iso-Butane, C_4H_{10} (*g*)	−4,160	Diethyl ether, $C_4H_{10}O$ (*l*)	−28,300
n-Pentane, C_5H_{12} (*g*)	−1,620	Benzene, C_6H_6 (*g*)	30,640
2-Methyl butane, C_5H_{12} (*g*)	−3,190	Benzene, C_6H_6 (*l*)	29,400
Tetramethyl methane, C_5H_{12} (*g*)	−3,310	Cyclohexane, C_6H_{12} (*l*)	6,800
		Cyclohexene, C_6H_{10} (*l*)	18,200
n-Hexane, C_6H_{14} (*g*)	80	Benzoic acid, $C_7H_6O_2$ (*s*)	−60,100
n-Heptane, C_7H_{16} (*g*)	1,750	Naphthalene, $C_{10}H_8$ (*s*)	45,200
n-Octane, C_8H_{18} (*g*)	3,400	Sucrose, $C_{12}H_{22}O_{11}$ (*s*)	−371,600
Ethylene, C_2H_4 (*g*)	16,279		

[1] The data are taken from different sources including, Pitzer, *Chem. Rev.*, **27,** 39 (1940), and Parks and Huffman, "Free Energies of Some Organic Compounds," Chemical Catalog Inc. Co., New York, 1932.

[2] Standard state = 1 gram-equivalent per liter

Example 23. Calculate from Table III the equilibrium constant for the following reaction at 25°.

$$2\text{HI}\ (g) = \text{H}_2\ (g) + \text{I}_2\ (s)$$

$$\Delta F^0 = 0 - 2 \times 315 = -630 \text{ cal}$$

$$= -1.987 \times 298.1 \times 2.303 \log K_p$$

$$K_p = \frac{p_{\text{H}_2} \times p_{\text{I}_2}}{p_{\text{HI}}{}^2} = \text{antilog} \frac{630}{1.987 \times 298.1 \times 2.303} = 2.90$$

Activities and Fugacities. Formulas 22 28 hold strictly only for ideal gases and dilute ideal solutions, but the equilibrium constant and its relation to free-energy change are so valuable that they are commonly used, even when the gases and solutions are not ideal. It is recognized that they are only approximately correct, but they are often sufficiently exact for practical purposes, particularly if the pressure is not greater than 1 atm and the concentration of nonelectrolytes not greater than 1 molal.

To make possible exact calculations, G. N. Lewis introduced the terms *fugacity* and *activity*, which are defined in such a way that the equilibrium constant is a true constant and is independent of the concentrations.

A good illustration of the difficulty of using pressures and concentrations is shown in the determination of the dissociation constant at 25° of N_2O_4, at different concentrations,* as given in **Fig. 68.** If N_2O_4

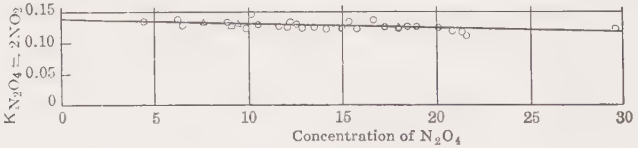


FIG. 68. Extrapolation of apparent equilibrium constants K_p to low pressures.

and NO_2 behaved as ideal gases, the values of the dissociation constant, calculated from $K_p = p_{NO_2}{}^2/p_{N_2O_4}$, should be independent of the pressure. Then, when K_p is plotted against the total pressure, a horizontal line should be produced. In Fig. 68 K_p is plotted against millimoles of gas per liter, calculated as N_2O_4, and it is evident that K_p increases as the total pressure is reduced. In the derivation of the relation, $\Delta F^0 = -RT \ln K_p$ it is assumed that the gases are ideal gases, and, accordingly, the correct value of K_p to use in thermodynamical calculations is the value extrapolated to zero pressure where the gases are strictly ideal. In this K_p has a value of 0.143 at zero pressure.

* Verhoek and Daniels, *J. Am. Chem. Soc.*, **53**, 1250 (1931).

Equation 23 was derived for ideal gases, and it does not apply to real gases, particularly at high pressures. It is convenient then to use a quantity *fugacity* * f instead of pressures which is defined arbitrarily by the equation:

$$F = RT \ln f + C \tag{29}$$

Another term of practical value in making use of these thermodynamic quantities is the *activity* a which is defined as the ratio of the fugacity f to the fugacity in some arbitrarily chosen standard state f^0

Thus

$$a = \frac{f}{f^0} \tag{30}$$

The activity or escaping tendency of a volatile liquid may be visualized as the tendency to pass off into the vapor state as measured approximately by its vapor pressure p_0. When a solute is added, the vapor pressure of the solvent p is decreased. The ratio p/p_0 is a measure of the escaping tendency of the solvent as compared to the escaping tendency in the pure liquid. It may be considered as describing approximately the *activity* of the solvent. For example, the vapor pressure of pure water at 25° is 23.7, and the partial pressure of water in a 10 per cent solution of sulfuric acid is 22.4. Then the relative escaping tendency or activity in solution is 22.4/23.7 or 0.95.

The change in free energy which occurs in going from the standard state to any other state is given by the expression:

$$\Delta F = F - F^0 = RT \ln f - RT \ln f^0 = RT \ln \frac{f}{f^0} = RT \ln a \tag{31}$$

For a solute, the standard state is usually taken as a hypothetical state in which the pure solute (that is, a solution in which $N_2 = 1$) would have the properties which the solute possesses at infinite dilution. The activity of a solute at any mole fraction is given by the expression, $a_2 = f_2/f_2{}^0$.

In Table IV the partial pressures of acetone and ether are given in millimeters at 30° for solutions of various mole fractions.†

* Fugacities of gases may be calculated from pressures by correcting for the deviations from ideal behavior at several pressures, and in different ways as given by Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," Chapter XVII, McGraw-Hill Book Co., New York, 1923; and by Hougen and Watson "Chemical Process Principles II Thermodynamics," John Wiley & Sons, New York, 1947.

† Sameshima, *J. Am. Chem. Soc.*, **40,** 1489 (1918).

TABLE IV

VAPOR PRESSURE OF ACETONE–ETHER SOLUTIONS AT 30°

Mole Fraction Ether N_1	Vapor Pressure Ether p_1	Mole Fraction Acetone N_2	Vapor Pressure Acetone p_2	$\frac{N_2}{p_2}$	Total Pressure $p_1 + p_2$
1.000	646.0	0.000	0	.....	646.0
0.961	623.5	0.0387	21.8	0.00177	645.3
0.867	570.8	0.133	66.2	0.00201	637.0
0.749	510.2	0.251	106.7	0.00235	616.9
0.504	390.3	0.496	167.5		557.8
0.349	301.5	0.651	201.2		502.7
0.295	266.0	0.705	213.7		479.7
0.162	166.5	0.838	243.1		409.6
0.066	71.0	0.934	266.8		337.8
0.047	55.3	0.953	270.7		326.0
0.020	20.8	0.980	276.6		297.4
0.000	0.0	1.000	282.7		282.7

If the acetone is considered to be the solute, the standard reference state is taken as a hypothetical acetone with the properties which it possesses as a solute at infinite dilution. Writing the equilibrium constant for the reaction

$$(CH_3)_2CO_{gas} = (CH_3)_2CO_{solution}$$

gives

$$K = \frac{a_{solution}}{a_{gas}} \tag{32}$$

The gas is sufficiently ideal so that no serious error is introduced by substituting the pressure of the gas for the activity. Since the solution is far from ideal, a considerable error would be introduced by substituting the mole fraction for the activity of acetone in solution, and K would not be the same at different concentrations. However, by writing

$$K' = \frac{N_2}{p_2} \tag{33}$$

and calculating the value of K' at several different concentrations, it is possible to extrapolate back to infinite dilution where the solution is ideal. This extrapolated value of K' is the true equilibrium constant

under conditions where the activity is equal to the mole fraction. This extrapolation is illustrated in **Fig. 69,** where it is found that K has the value 0.001697.

Since K has been evaluated, it is now possible with the help of equation 33 to determine the activity of acetone at any concentration from its vapor pressure. Thus, at a mole fraction of 0.251, the partial vapor pressure is 106.7, and its activity in solution is given by the relation:

$$a_2 = 0.001697 \times 106.7 = 0.181$$

The fact that the activity of acetone is less than its mole fraction means that its escaping tendency (represented approximately by its vapor

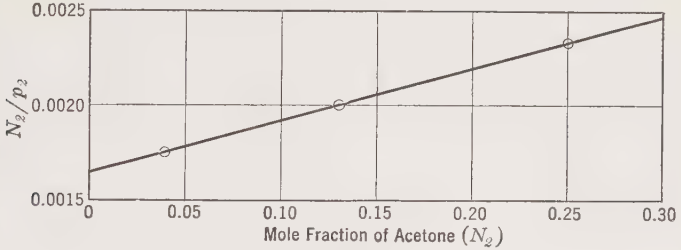


FIG. 69. Evaluation of equilibrium constant for acetone vapor and liquid acetone in infinitely dilute ether solution.

pressure) is less than if the acetone retained in this solution the properties which it possesses in an extremely dilute solution in ether.

If ether is considered to be the solvent, its activity at any mole fraction is simply the ratio of the partial pressure to the vapor pressure of pure ether, which is 646.0 mm. For example, the partial pressure of ether at 0.295 mole fraction is 266.0 mm, and the activity of the ether is 266.0/646.0 or 0.412. If the solution were ideal, the activity would be 0.295.

Of course it is quite arbitrary to take ether as the solvent and acetone as the solute; equally useful results would be obtained if ether were considered to be the solute. The standard state adopted should be specified, but in calculations involving only changes in concentration the standard state cancels out.

It may be suggested that nothing is gained by the introduction of these arbitrary quantities, fugacity and activity—that the ability thus acquired to express laboratory facts with simple formulas is artificial. However, a great gain is made in a practical way. The relation between activities and concentration may be determined empirically for a given substance by independent experimental measurements, and then many

of the useful formulas of thermodynamics may be applied with exactness. Particularly in the study of electrolytes where the electric charges cause large deviations from ideal behavior, it is necessary to use activities even in fairly dilute solutions.

Methods for determining activities of electrolytes and other solutes are described and illustrated in the appendix on pages 682 to 688.

Influence of Temperature on Chemical Equilibrium. According to equation 24 for ideal gas systems,

$$-\Delta F^0 = RT \ln K_p$$

Differentiating with respect to temperature gives

$$\frac{-d\ \Delta F^0}{dT} = R \ln K_p + RT \frac{d \ln K_p}{dT} \tag{34}$$

According to the Gibbs–Helmholtz equation * (page 161):

$$\Delta F^0 - \Delta H = T \frac{d\ \Delta F^0}{dT} \tag{35}$$

Substituting in equation 35 the value of $d\ \Delta F^0/dT$ obtained in equation 34

$$\Delta H - \Delta F^0 = RT \ln K_p + RT^2 \frac{d \ln K_p}{dT} \tag{36}$$

Adding equation 24 to equation 36 and rearranging, we have

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2} \tag{37}$$

This is a very important equation which is used for calculating heats of reaction from chemical equilibria, and for calculating equilibrium constants at different temperatures. The Clausius–Clapeyron equation, discussed on page 177 is a special case of this more general equation. In fact, the equilibrium constant K_p can be extended to include any type of equilibrium such as reactions of gases or solutes, vaporization of liquids, and sublimation or solubility of solids.

For equilibria in solutions (at constant pressure) equation 37 is written

$$\frac{d \ln K_c}{dT} = \frac{\Delta H}{RT^2} \tag{38}$$

* Since the pressures are constant for ΔF^0, partial differentiation holding p constant has been replaced by ordinary differentiation.

For gaseous equilibria, where $K_p = K_c(RT)^{\Delta n}$ it can be proved that

$$\frac{d \ln K_c}{dT} = \frac{\Delta E}{RT^2} \tag{39}$$

If the temperature range is small, or if the heat capacities of reactants and products are nearly the same, ΔH can be assumed to be constant, and integration of equation 37 gives

$$\ln K_p = -\frac{\Delta H}{R}\frac{1}{T} + C \tag{40}$$

Data are given in Table V for the equilibrium constant at different temperatures for the reaction $N_2 + O_2 \rightleftarrows 2NO$. Given also are the

TABLE V

Equilibrium Constants for the Reaction $N_2 + O_2 \rightleftarrows 2NO$ and Equilibrium Pressures of Nitric Oxide

Temperature, °K	K_p atm $\times 10^4$	Partial Pressures of NO in Atmospheres		
		$p_{N_2} = 0.8$ $p_{O_2} = 0.2$	$p_{N_2} = 0.8$ $p_{O_2} = 0.1$	$p_{N_2} = 0.8$ $p_{O_2} = 0.05$
1800	1.21	0.44	0.31	0.22
1900	2.31	0.61	0.43	0.31
2000	4.08	0.81	0.57	0.40
2100	6.86	1.05	0.74	0.53
2200	11.00	1.33	0.94	0.67
2300	16.90	1.64	1.16	0.82
2400	25.10	2.00	1.42	1.00
2500	36.00	2.40	1.70	1.20
2600	50.30	2.84	2.01	1.42
2700	68.70	3.32	2.34	1.66

partial pressures of nitric oxide in equilibrium with air and with mixtures of nitrogen and varying amounts of oxygen. The equilibrium pressures of nitric oxide are proportional to the square roots of the pressures of oxygen when the pressure of nitrogen is kept constant.

In **Fig. 70** the values of log K_p are plotted against $1/T$, and it is evident that a straight line is produced. Such a result is to be expected from equation 40, and, in fact, the heat of dissociation ΔH can be calculated from the slope of the line, as follows:

$$\Delta H = -\text{slope} \times 2.303R \tag{41}$$

For this reaction ΔH is 43,520, since the slope is $-9{,}510$ and R is 1.987 cal.

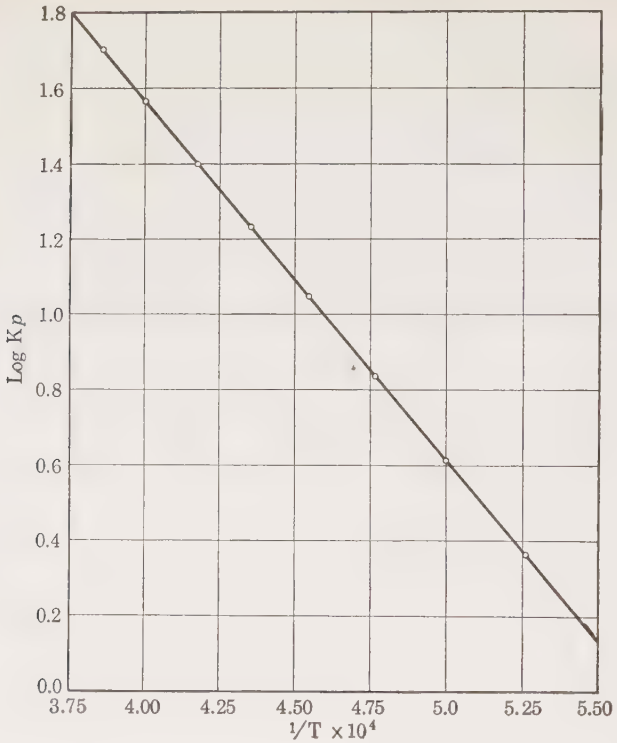


FIG. 70. Log K_p plotted against $1/T \times 10^4$ for the formation of nitric oxide. The heat of reaction is calculated from the slope of the straight line.

The value of the integration constant C in equation 40 can be determined from experimental values of K_p at definite temperatures, and the practical working equation becomes

$$\log K_p = \frac{-43{,}520}{2.303 \times 1.987T} + 1.365$$

Equation 37 can be solved also by integrating between limits K_{p_2} at T_2 and K_{p_1} at the lower temperature T_1, as was done on page 178.

$$\ln K_{p_2} - \ln K_{p_1} = \frac{-\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^0}{2.303R}\left(\frac{T_2 - T_1}{T_2 \times T_1}\right) \qquad (42)$$

Example 24. Calculate the heat of dissociation of nitric oxide from the data at 2000° K and 2500° K given in Table V.

$$\log \frac{K_{p_2}}{K_{p_1}} = \log \frac{0.00360}{0.000408} = \frac{\Delta H}{2.303 \times 1.987} \left(\frac{2500 - 2000}{2500 \times 2000} \right)$$

and

$$\Delta H = 43{,}300$$

Example 25. The equilibrium constant K_p for the reaction,

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

is 10.0 at 690° K. The heat of the reaction ΔH is $-10{,}200$ cal. Calculate the partial pressure of each of the gases in an equilibrium mixture prepared by mixing 0.400 mole of CO and 0.200 mole of H_2O in a volume of 5 liters at 500° K.

$$\log \frac{K_{690^\circ \text{K}}}{K_{500^\circ \text{K}}} = \frac{-10{,}200(690 - 500)}{2.303 \times 1.987 \times 500 \times 690} = -1.2275$$

$$\log K_{500^\circ \text{K}} = \log 10.0 + 1.2275 = 2.2275 \qquad K_{500^\circ \text{K}} = 169$$

Let x = number of moles of CO_2 and H_2 produced.

$$K_p = 169 = \frac{\left(x \frac{RT}{v}\right)\left(x \frac{RT}{v}\right)}{\left[(0.4 - x)\frac{RT}{v}\right]\left[(0.2 - x)\frac{RT}{v}\right]} = \frac{x^2}{(0.4 - x)(0.2 - x)}$$

$$x = 0.199$$

$$p_{CO_2} = p_{H_2} = \frac{nRT}{v} = \frac{0.199 \times 0.08205 \times 500.0}{5} = 1.63 \text{ atm}$$

$$p_{CO} = \frac{(0.4 - 0.199) \times 0.08205 \times 500.0}{5} = 1.65 \text{ atm}$$

$$p_{H_2O} = \frac{(0.2 - 0.199) \times 0.08205 \times 500.0}{5} = 0.01 \text{ atm}$$

If the heat of reaction at constant pressure is zero, the right-hand sides of equation 37 or 38 becomes equal to zero. In other words, in such a reaction a change in temperature does not cause a displacement of the equilibrium.

The reaction of acetic acid and ethanol is an example of a reaction in which very little heat is evolved. Accordingly, the equilibrium constant should have practically the same value at all temperatures. Experimental measurements show that this is indeed the case.

Influence of Temperature on Free-Energy Changes. We have just seen how to calculate equilibrium constants at a specified temperature if we know the equilibrium constants at two different temperatures or

if we know the equilibrium constant at one temperature and in addition know the heat of reaction. Another approach to the same problem is through the calculation of the free-energy change for the reaction at a specified temperature. Knowing ΔF^0, we can then calculate K from the important relation $\Delta F^0 = -RT \ln K$.

In the present section we will show how to calculate the change with temperature of ΔF^0 from a knowledge of the heat of reaction and the heat capacities of products and reactants. Often the free energies of formation $\Delta F_f{}^0$ and the heats of formations ΔH_f and the heat capacities are known at 25°, and it is desired to calculate ΔF^0 at high temperatures. In order to obtain a formula for calculating free-energy changes at different temperatures, we first differentiate $\Delta F/T$ with respect to temperature at constant pressure, thus:

$$\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T} = \frac{T\frac{\partial(\Delta F)}{\partial T} - \Delta F\frac{\partial T}{\partial T}}{T^2} \tag{43}$$

But, according to the Gibbs–Helmholtz equation derived on page 161, at constant pressure,

$$\frac{\partial(\Delta F)}{\partial T} = \frac{\Delta F}{T} - \frac{\Delta H}{T} \tag{44}$$

Substituting into equation 43, we have

$$\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T} = \frac{T\left(\frac{\Delta F}{T} - \frac{\Delta H}{T}\right) - \Delta F}{T^2} = -\frac{\Delta H}{T^2} \tag{45}$$

But ΔH depends on the temperature and on the difference between the heat capacity of the products and the reactants (page 137), as shown in the equation,

$$\Delta H = \Delta H_0 + \int \Delta C_p \, dT \tag{46}$$

where ΔH_0 is an integration constant, a hypothetical heat of reaction at absolute zero, if it is assumed that the heat capacity relations, determined at ordinary temperatures, hold down to absolute zero. The heat capacity of a substance can usually be expressed by an empirical equation of the type,

$$C_p = \Gamma_0 + \Gamma_1 T + \Gamma_2 T^2 + \cdots \tag{47}$$

where the Γs represent empirical constants. Since the difference between the heat capacity of the reactants and the products is ΔC_p,

$$\Delta C_p = C_{p\ (\text{products})} - C_{p\ (\text{reactants})} = \Delta\Gamma_0 + \Delta\Gamma_1 T + \Delta\Gamma_2 T^2 + \cdots \quad (48)$$

On substituting into equation 46 and integrating, we get

$$\Delta H = \Delta H_0 + \int \Delta C_p\, dT = \Delta H_0 + \Delta\Gamma_0 T + \tfrac{1}{2}\Delta\Gamma_1 T^2 + \tfrac{1}{3}\Delta\Gamma_2 T^3 + \cdots \quad (49)$$

and, again, substituting equation 49 into equation 45,

$$\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T} = \frac{-\Delta H}{T^2} = \frac{-\Delta H_0 - \Delta\Gamma_0 T - \frac{1}{2}\Delta\Gamma_1 T^2 - \frac{1}{3}\Delta\Gamma_2 T^3 - \cdots}{T^2} \quad (50)$$

On integrating, we have

$$\frac{\Delta F}{T} = \frac{\Delta H_0}{T} - \Delta\Gamma_0 \ln T - \tfrac{1}{2}\Delta\Gamma_1 T - \tfrac{1}{6}\Delta\Gamma_2 T^2 \cdots + I \quad (51)$$

and

$$\Delta F = \Delta H_0 - \Delta\Gamma_0 T \ln T - \tfrac{1}{2}\Delta\Gamma_1 T^2 - \tfrac{1}{6}\Delta\Gamma_2 T^3 \cdots + IT \quad (52)$$

The integration constant ΔH_0 may be evaluated by the experimental determination of ΔH at some temperature; and the integration constant I may be evaluated by the experimental determination of ΔF at a definite temperature.

Example 26. Calculate the free energy of formation of hydrochloric acid at 1327° or 1600° K from the free energy and heat of reaction at 25°.

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 = HCl, \qquad \Delta F^0_{298\ K} = -22{,}692, \qquad \Delta H_{298\ K} = -22{,}063$$

By equation 46,

$$\Delta H_0 = \Delta H - \int_0^T \Delta C_p\, dT$$

According to the empirical equations for the heat capacities of gases (page 135)

$$\Delta C_p = C_{p,HCl} - (\tfrac{1}{2}C_{p,H_2} + \tfrac{1}{2}C_{p,Cl_2}) = 6.70 + 0.00084T - \left(\frac{6.62 + 0.00081T}{2} + \frac{8.28 + 0.00056T}{2}\right) = -0.75 + 0.000155T$$

$$\Delta H_0 = -22{,}063 + 0.75 \times 298 - \tfrac{1}{2} \times 0.000155 \times 298^2 = -22{,}063 + 224 - 7 = -21{,}846$$

Substituting in equation 52 yields

$$-22{,}692 = -21{,}846 + 0.75 \times 298 \times 2.303 \times 2.474 - \tfrac{1}{2} \times 0.000155 \times 298^2 + 298I$$

$$I = \frac{-22{,}692 + 21{,}846 - 1273 + 7}{298} = -7.087$$

and

$$\Delta F^0 = -21{,}846 + 0.75T \ln T - 7.75 \times 10^{-5}T^2 - 7.087T$$

This general equation may now be used to calculate the free energy of formation of hydrochloric acid at any temperature for which the heat capacity equations are valid.

$$\Delta F^0_{1600\,\mathrm{K}} = -21{,}846 + 0.75 \times 1600 \times 2.303 \times 3.204 - 7.75 \times 10^{-5} \times 1600^2 - 7.087 \times 1600 = -24{,}528$$

Hydrochloric acid is less stable at the higher temperature. This difference in stability is easily seen by comparing the equilibrium constants.

At 25°, $\Delta F^0 = -22{,}692$ and $K = 4.3 \times 10^{16}$, whereas at 1327°, $\Delta F^0 = -24{,}528$ and $K = 2.2 \times 10^3$.

Calculations of Equilibrium Constants from Enthalpy and Entropy. The relation between the entropy change and free-energy change in an isothermal reaction was given in equation 20 of Chapter VIII:

$$\Delta F = \Delta H - T\,\Delta S \qquad (53)$$

It is evident that, when there is no change in entropy during a reaction, the change in enthalpy is equal to the change in free energy. Usually, however, there is an entropy change during the reaction, and the decrease in free energy is greater or less than the decrease in enthalpy, depending on the sign of ΔS.

Since entropies and heats of reaction can be determined from calorimetric measurements alone, it is now possible to calculate free-energy changes and equilibrium constants without involving any chemical measurements. This determination of chemical affinities from thermal data is a goal which was eagerly sought by many early investigators.

The calculation of chemical equilibria from entropy data using equation 53 and equation 10 of Chapter VIII is particularly valuable in organic chemistry because frequently no other method is available. Often the reaction rates are so very slow that direct measurements of equilibrium are impossible. Methane may be taken as an example. Methane appears to be a stable substance at room temperature, and carbon and hydrogen appear to be unreactive toward each other. It is not possible then to measure the equilibrium among the three at low

temperatures, but it may be determined indirectly from the entropies and the heat of reaction.

Example 27. Calculate from thermal data alone the equilibrium constant of the following reaction at 600°:

$$C_{graphite} + 2H_2\ (g) = CH_4\ (g) \qquad \Delta H_{873} = -21{,}045$$

The entropies of $C_{graphite}$, H_2, and CH_4 are 4.8, 38.9, and 56.6, respectively, at 873° K and 1 atm.

$$\Delta S = S_{products} - S_{reactants} = 56.6 - (38.9 \times 2 + 4.8) = -26.0$$

$$\Delta F^0 = \Delta H - T\,\Delta S = -21{,}045 - [873 \times (-26)] = 1653$$

Since

$$\Delta F^0 = -RT \ln K$$

$$K = 0.386$$

This method of calculating equilibrium constants from entropy data has come into extensive industrial use, particularly in determining whether or not a given synthesis is thermodynamically possible.

The limiting factor in many calculations of this type is the low accuracy with which the heats of reactions are known. These values are usually obtained from differences between large quantities, and a small error in one of these values makes a large error in the value of ΔF. In the calculation of the methanol equilibrium, for example, an error of 0.1 per cent in one of the values for the heat of combustion makes an error of 35 per cent in the equilibrium constant. For a time the validity of the third law itself was questioned because of the large discrepancy between the calculated and observed equilibrium in the methanol synthesis. This discrepancy was finally traced to a considerable error in the heat of combustion of methanol. As a rule, a greater error can be tolerated in the entropy measurements than in the measurements which determine the values of the enthalpy.

Many new measurements of entropies and free energies are being recorded in the current literature, and tables of reliable data will ultimately make possible the calculation of most equilibrium constants. Parks and Huffman * gave an excellent collection of the data for organic compounds available up to 1932, together with theoretical discussions and examples of the use of these data. A very helpful collection of data and techniques for calculating thermodynamic data has been written by Wenner.† Semiempirical and theoretical methods are

* Parks and Huffman, "Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932.

† Wenner, "Thermochemical Calculations," McGraw-Hill Book Co., New York, 1941.

given for estimating specific heat and other important constants from meager data.

When data are not available for certain compounds it is still possible to estimate free energies and entropies, using empirical rules based on the molecular structures. For example, when CH_3 is substituted for a hydrogen atom, attached to a chain, the molar free energy of formation at 25°, $\Delta F^0_{298\,K}$ is increased by about 1900 cal; when C_2H_5 is substituted, it is increased by 3000 cal. In a similar way the substitution of a hydrogen atom by an OH group to form a primary alcohol gives a change in $\Delta F^0_{298\,K}$ of $-34{,}000$; Cl for H gives a change of -1600; NH_2 for H gives a change of 6000; and NO_2 for H gives a change of 7000. For example, if $\Delta F^0_{298\,K}$ of C_2H_6 is known to be $-10{,}700$, $\Delta F^0_{298\,K}$ of C_2H_5OH should be about $(-10{,}700 - 34{,}000)$, or $-44{,}700$. Experimental measurements give $-40{,}200$ cal.*

Useful rules for estimating enthalpies, entropies and free energies are given by Hougen and Watson.* Extensive tables of enthalpies, entropies, and free energies at different temperatures, are now becoming available.† Special attention has been paid to the hydrocarbons.

Equilibria between Solids and Gases. The calculation of an equilibrium constant is simplified if one or more of the substances taking part in the equilibrium is a solid or a liquid. As long as the solid or liquid is present, the partial pressure of the gas remains fixed and equal to the vapor pressure. Moreover, this pressure is independent of the amount of solid or liquid present. This constant pressure can then be incorporated in the equilibrium constant. Pure solids and liquids and the vapors in equilibrium with them are usually assigned activities of unity, and so they can be neglected in writing the expression for the equilibrium constant. Thus, for the reaction,

$$CaCO_3\,(s) \rightleftharpoons CaO(s) + CO_2\,(g)$$

the equilibrium constant may be written

$$K_p' = \frac{p_{CaO} \times p_{CO_2}}{p_{CaCO_3}}$$

Since p_{CaO} and p_{CaCO_3} are constant at any one temperature, they do not really affect the equilibrium, and the constant K_p is used where

$$K_p = p_{CO_2} \tag{54}$$

* Hougen and Watson, "Chemical Process Principles Part II. Thermodynamics," John Wiley & Sons, New York, 1947.

† Rossini and associates, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1947, and American Petroleum Institute Research Project 44.

The relation between K_p and K_p' is

$$K_p = K_p' \frac{p_{CaCO_3}}{p_{CaO}}$$

The equilibrium constant, at any one temperature, is determined solely by the pressure of the carbon dioxide evolved. Table VI gives the values of the pressure of carbon dioxide corresponding to various temperatures.

TABLE VI

Dissociation Pressures of $CaCO_3$

Temperature, °C	Pressure, atm
500	0.000096
600	0.00242
700	0.0292
800	0.220
897	1.000
1000	3.871
1100	11.499
1200	28.680

When solid ammonium hydrosulfide is heated, it is almost completely dissociated into ammonia and hydrogen sulfide, as shown by the following equation:

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$$

This reaction was investigated by Isambert, who found that the total gas pressure at 25.1° is equal to 0.66 atm. Writing an equilibrium constant for this reaction and remembering that p_{NH_4HS}, the vapor pressure of the solid ammonium hydrosulfide, is constant, we have

$$K_p' = \frac{p_{NH_3} \times p_{H_2S}}{p_{NH_4HS}} \qquad K_p = p_{NH_3} \times p_{H_2S}$$

where K_p is a constant at a given temperature.

The total pressure P must be equal to the sum of the partial pressures, but the NH_4HS is so largely dissociated that its pressure can be neglected. Then:

$$P = p_{NH_3} + p_{H_2S} + p_{NH_4HS} \cong p_{NH_3} + p_{H_2S}$$

It must be clearly understood that p_{NH_4HS} is neglected in determining the total pressure because it is small, but that it disappears in the equilibrium constant K not because it is small but because it is *constant.* Hence, since $p_{NH_3} = p_{H_2S}$,

$$\frac{p}{2} = \frac{0.66}{2} = 0.33 = p_{NH_3} = p_{H_2S}$$

$$K_p = 0.33 \times 0.33 = 0.109$$

Table VII gives various values of the equilibrium constant calculated from experiments in which an excess of H_2S or NH_3 was added to the dissociated NH_4HS vapor.

TABLE VII

EQUILIBRIUM PRESSURES OF NH_4HS (25.1°)

Pressure of Ammonia	Pressure of Hydrogen Sulfide	$p_{NH_3} \times p_{H_2S} = K_p$
0.274	0.387	0.106
0.182	0.603	0.110
0.549	0.192	0.105
0.596	0.188	0.112
		Mean 0.108

As will be seen, the mean value of the equilibrium constant agrees well with the value found for equivalent amounts of the products of dissociation.

The dissociation of ammonium carbamate takes place according to the equation:

$$OC\begin{matrix}ONH_4\\ \diagdown\\ \diagup\\ NH_2\end{matrix} \rightleftharpoons 2NH_3 + CO_2$$

This dissociation has been very carefully investigated by Briggs and Migrdichian.*

If we omit the vapor pressure of the solid, $p_{NH_4OCONH_2}$ because it is a constant in the presence of the solid compound:

$$K_p = p_{NH_3}{}^2 \times p_{CO_2} \qquad (55)$$

* Briggs and Migrdichian, *J. Phys. Chem.*, **28**, 1121 (1924).

The total pressure P is due to 3 moles of gas ($2NH_3 + CO_2$), since the small vapor pressure of the solid may be neglected at room temperature. Then,

$$p_{NH_3} = \tfrac{2}{3}P \quad \text{and} \quad p_{CO_2} = \tfrac{1}{3}P$$

and when P refers only to gases in which $p_{NH_3} = 2p_{CO_2}$, equation 55 becomes

$$K_p = \frac{4P^3}{27}$$

At a definite temperature K_p has a fairly constant value even when an excess of ammonia or carbon dioxide is added.

Example 28. For the reaction $C\,(s) + 2H_2 \rightleftharpoons CH_4$ at 1000°, $K_p = 0.263$. Calculate the total pressure at equilibrium when 0.100 mole of CH_4 is placed in a volume of 2 liters at 1000°. Let x = the number of moles of CH_4 which dissociate.

$$p_{CH_4} = \frac{nRT}{v} = \frac{(0.1 - x)(0.08205)(1273)}{2} = 5.22 - 52.2x$$

$$p_{H_2} = \frac{nRT}{v} = \frac{2x(0.08205)(1273)}{2} = 104x$$

$$K_p = 0.263 = \frac{p_{CH_4}}{p_{H_2}{}^2} = \frac{5.22 - 52.2x}{(104x)^2} \qquad x = 0.035$$

$$p_{CH_4} = \frac{(0.1 - 0.035)(0.08205)(1273)}{2} = 3.4$$

$$p_{H_2} = \frac{2(0.035)(0.08205)(1273)}{2} = 3.7$$

$$\text{Total pressure} = 3.4 + 3.7 = 7.1 \text{ atm}$$

Influence of Temperature on Equilibria between Solids and Solutions. When a liquid or solid is surrounded by gaseous space, molecules leave the liquid or solid and build up a gaseous pressure which increases until a state of equilibrium is attained such that the rate at which molecules return to the surface is equal to the rate at which molecules leave it. These equilibrium pressures are called vapor pressures and sublimation pressures. In a similar manner, when a solid is surrounded by liquid, molecules pass out into the liquid and increase in concentration until an equilibrium is established at which the rate of deposition is equal to the rate of solution. This equilibrium concentration is known as the solubility. As long as solid solute is in contact with the solution, the concentration is fixed at the saturation concentration or solubility. The equilibrium constant then is the solubility expressed in molalities

or mole fractions; and sometimes in moles per liter. The solubility of a slightly soluble liquid may be treated in the same way as the solubility of a solid. The concentration of the solute in the surrounding solvent is usually very much greater than it would be in an evacuated space, because the solvent molecules exert an attraction for the solute molecules. Then, for the equilibrium,

$$A_{\text{solid}} \rightleftharpoons A_{\text{solution}}$$

$$K_c = c_{\text{sat. solution}} = s \tag{56}$$

where s is the solubility expressed as molality $m_{\text{sat.}}$ or mole fraction $N_{2\text{sat.}}$. Then, according to equation 38,

$$\frac{d \ln N_{2\text{sat.}}}{dT} = \frac{\Delta H_{\text{sat.}}}{RT^2} \tag{57}$$

or

$$\frac{d \ln m_{\text{sat.}}}{dT} = \frac{\Delta H_{\text{sat.}}}{RT^2} \tag{58}$$

Equation 57 is an exact equation for ideal solutions in which $\Delta H_{\text{sat.}}$ is the heat of solution of the solute in the saturated solution. It is clear that for nonideal solutions more complicated equations will be required which allow for the change in activity with the concentration and with the temperature.*

Equilibria of a Solute in Two Immiscible Solvents. If a solid (or liquid) is soluble in two different liquids which do not mix with each other and an excess of solute is added to the two liquids in contact, each becomes saturated and the concentrations in the two immiscible solutions will be different, depending on the relative solubilities.

In unsaturated solutions there is also a definite equilibrium of solute between the two immiscible solvents. The solute will distribute itself between the two solvents until equilibrium is reached, and the rate of passage of molecules across the surface between the two liquids is the same from the first solvent to the second as it is from the second solvent to the first. This ratio of concentrations in the two solutions is known as the distribution ratio or sometimes as the distribution coefficient. Then,

$$K_c = \frac{c_2}{c_1} \tag{59}$$

where c_2 and c_1 are the concentrations in the two solvents.

* Williamson, The Exact Calculation of Heats of Solution from Solubility Data. *Trans. Farad. Soc.*, **40**, 421 (1944).

This distribution ratio K_c would be the same as the ratios of the solubilities $K_{csat.}$ if both the solutions were ideal. However, there is usually interaction between solute and solvent which is not the same in the two solvents and which changes with the concentration. Particularly if the solute is highly soluble, the value of K_c in dilute solutions will depart considerably from the value of $K_{csat.}$, but over comparatively small concentration ranges equation 59 can be applied for most practical purposes, as shown in Table VIII.

TABLE VIII

Distribution of Bromine between Water and Bromoform

Moles per liter in water	0.0075	0.015	0.022	0.029	0.036
Moles per liter in bromoform	0.5	1.0	1.5	2.0	2.5
$K_c = \frac{c_{CHBr_3}}{c_{H_2O}}$	66.7	68.2	68.7	68.8	68.9

If the solute possesses a different molecular weight in the two solvents, a complication is introduced, and K as given in equation 59 may change considerably as the concentration is changed. One example is the distribution of electrolytes between water and an insoluble organic liquid such as benzene. Hydrochloric acid dissolves in water to give H^+ and Cl^- ions, but in benzene it is not dissociated. In other cases, as, for example, benzoic acid, the molecules associate in nonpolar solvents like benzene to give double molecules as determined by boiling-point or freezing-point measurements (page 233), but they do not associate in polar solvents like water or ether.

If a substance is associated into a double molecule in one solvent but has a normal molecular weight (equal to the sum of the atomic weights) in the other, the equilibrium may be written $A_2 \rightleftharpoons 2A$, and the equilibrium constant is given by the formula:

$$K_c = \frac{c_A{}^2}{c_{A_2}} \tag{60}$$

In the more general case where the molecule associates into n molecules $A_n \rightleftharpoons nA$, and

$$K_c = \frac{c_A{}^n}{c_{A_n}} \tag{61}$$

The properties of mixed solutes are additive in dilute solutions, each solute behaving as if the other were not present. In some cases and particularly in concentrated solutions, however, the presence of other solutes may profoundly affect the distribution ratio either by forming

some complex compound between the solutes or by combining with the solvent molecules and thus changing the character of the solvent. A common example of the latter procedure is the "salting out" in solvent extraction. Certain organic material for example can be removed from water by repeated extractions with ether, but the extraction can be improved by saturating the water with sodium chloride or other salt which does not dissolve in the ether. A similar case was discussed on page 204.

Extraction with immiscible solvents is an important operation which finds many practical applications in organic chemistry, in biochemistry and in inorganic chemistry. Organic compounds are frequently more soluble in organic solvents than in water and can be removed from water by shaking with hydrocarbons or other immiscible organic liquids. Proteins and other compounds in plant and animal products can be separated by suitable choice of solvent and electrolyte concentration. Several inorganic salts, like ferric chloride, are soluble in organic solvents. A separation can then be effected from salts of metals such as potassium which are not soluble. Choice of solvent, addition of "salting out" solutes, change of valence, and use of "complexing" agents are some of the variables which can be used to increase the efficiency of the separations.

The greater the surface area exposed between the two liquids, the more rapidly will equilibrium be achieved. The equilibrium will not be affected, but the time taken to effect a separation can be greatly reduced. Accordingly, it is common practice to shake the two solutions together. The most effective separation involves flowing two different immiscible solvents of different densities in opposite directions through tall towers filled with special packing to give a large surface like the fractionation towers used for separating liquids by vaporization and condensation. These packed towers are equivalent to a large number of batch extractions, and, like any continuous process, they are preferred for industrial or large-scale operations. The number of theoretical plates equivalent to the number of batch operations replaced can be calculated for a solvent extraction tower in much the same manner that the number of theoretical plates is calculated for a fractionating column.

REFERENCES

Glasstone, "Thermodynamics for Chemists," D. Van Nostrand Co., New York, 1947.

Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, 1946, Chapter XI.

Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, Chapter XXIV.

PARKS and HUFFMAN, "The Free Energy of Some Organic Compounds," Chemical Catalog Co., New York, 1932.
WENNER, "Thermochemical Calculations," McGraw-Hill Book Co., New York, 1941.
KELLEY, IX. The Entropies of Inorganic Substances, *Bur. Mines Bull. 434*, 1941.
MACDOUGALL, "Thermodynamics and Chemistry," John Wiley & Sons, New York, 1939.
STEINER, "Introduction to Chemical Thermodynamics," McGraw-Hill Book Co., New York, 1941.
HOUGEN and WATSON, "Chemical Process Principles, Part II, Thermodynamics," John Wiley & Sons, New York, 1947.
PITZER, *Chem. Rev.*, **27**, 39 (1940).
ROSSINI and associates, "Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, Washington, D. C., 1947.

PROBLEMS

1. Sulfur trioxide dissociates according to the reaction:

$$2SO_3 \rightarrow 2SO_2 + O_2$$

At 630° the density of the partially dissociated gases is 0.000927 g per milliliter. Calculate (*a*) the degree of dissociation of SO_3 into SO_2 and O_2, (*b*) the equilibrium constant of the reaction. *Ans.* (*a*) 0.332. (*b*) 0.0441.

2. For the gaseous reaction $COCl_2 \rightleftharpoons CO + Cl_2$ at 100°, the dissociation constant K_p is 6.7×10^{-9}. Calculate the partial pressure of carbon monoxide in equilibrium with phosgene at this temperature under a total pressure of 2 atm. The dissociation is so slight that the partial pressure of phosgene may be taken as equal to the total pressure. *Ans.* 1.16×10^{-4} atm.

3. For the reaction $2HI \rightleftharpoons H_2 + I_2$ at 698.6° K, $K_p = 1.83 \times 10^{-2}$. (*a*) How many grams of hydrogen iodide will be formed when 10 g iodine and 0.1 g of hydrogen are heated to this temperature in a 2-liter vessel? (*b*) What will be the partial pressures of H_2, I_2, and HI? *Ans.* (*a*) 8.70. (*b*) H_2, 0.448; I_2, 0.155; HI, 1.95 atm.

4. When 0.00645 mole of amylene and 0.001 mole of acetic acid are mixed in 845 ml of an inert solvent, 0.000784 mole of ester is formed according to the reaction:

$$CH_3COOH + C_5H_{10} \rightleftharpoons CH_3COOC_5H_{11}$$

How much ester will be formed when one mixes 0.00584 mole of amylene and 0.001 mole of acetic acid in 575 ml? *Ans.* 0.000826.

5. From the table of free energies of formation state whether the reaction,

$$CO\ (g) + PbO\ (s) = CO_2\ (g) + Pb\ (s)$$

can proceed at 25°, and calculate the equilibrium constant.

Ans. Yes. $K = 1.0 \times 10^{12}$.

6. Determine (*a*) $\Delta\overset{\frown}{F^0}$ and (*b*) the equilibrium constant at 298° K for the reaction,

$$CO_2 + H_2 = H_2O + CO$$

from the following data:

$$CO_2\ (g) + 4H_2\ (g) = CH_4\ (g) + 2H_2O\ (g) \qquad \Delta F^0_{298K} = -26{,}912$$
$$2H_2\ (g) + O_2\ (g) = 2H_2O\ (g) \qquad \Delta F_{298K} = -109{,}014$$

$2C\,(s) + O_2\,(g) = 2CO\,(g)$ $\quad \Delta F^\circ_{298K} = -65{,}020$

$C\,(s) + 2H_2\,(g) = CH_4\,(g)$ $\quad \Delta F^\circ_{298K} = -12{,}206$

Ans. (*a*) 7,291. (*b*) 4.5×10^{-6}.

7. For the reaction, $A + B \rightarrow AB$, $\Delta F^0 = -2000$ cal at 27°. Under what total pressure must an equimolecular gaseous mixture be placed in order to produce a 40 per cent conversion into AB? *Ans.* 0.062 atm.

8. Because of dissociation, the molecular weight of N_2O_4 is not 92.02 but somewhere between 92.02 and 92.02/2, depending on the temperature and pressure. The reaction is $N_2O_4 \rightleftharpoons 2NO_2$. The average molecular weights M_{avg} under one atmosphere total pressure and at different temperatures are as follows:

$t°$	15°	35°	55°
M_{avg}	82.00	72.45	61.24

Calculate the degree of dissociation and the equilibrium constant K at each of these temperatures.

(*a*) Plot log K against $1/T$, and determine ΔH for the dissociation of N_2O_4.

(*b*) Calculate the equilibrium constant at 25°.

(*c*) Calculate the degree of dissociation α at 25° when the total pressure is 1 atm.

Ans. (*a*) 14.600. (*b*) 0.141. (*c*) 0.185.

9. ΔH for the gaseous reaction $C_2H_2 + D_2O \rightleftharpoons C_2D_2 + H_2O$ is 530 cal. At 25° K_p is 0.82. How much C_2D_2 is formed if 1 mole of C_2H_2 and 2 moles of D_2O are put together at a total pressure of 1 atm and at 100°? Assume that the reactants and products have equal heat capacities and behave as perfect gases. *Ans.* 0.66.

10. In a study of the formation of methane from hydrogen and graphite Storch used the following data:

For hydrogen (H_2) $\quad C_p = 6.85 + 0.00028T + 0.00000022T^2$

$S_{298K} = 31.23$

For graphite (C) $\quad C_p = 1.22 + 0.00489T - 0.00000111T^2$

$S_{298K} = 1.3$

For methane (CH_4) $\quad C_p = 4.38 + 0.01417T$

$S_{298K} = 43.39$

(*a*) Calculate the entropies of each of these substances at 873° K at constant pressure.

(*b*) Calculate ΔS^0_{873K} for the reaction

$$C_{graphite} + 2H_2\,(g) \rightarrow CH_4\,(g)$$

Ans. (*a*) Hydrogen, $S_{873K} = 38.82$; graphite, $S_{873K} = 5.04$; methane, $S_{873K} = 56.25$.

(*b*) −26.4 cal per degree.

11. (*a*) From the data of the preceding problem calculate ΔC_p for the reaction:

$$C_{graphite} + 2H_2\,(g) \rightarrow CH_4\,(g)$$

(*b*) Find an equation expressing ΔH^0 as a function of temperature. ΔH^0_{298K} for this reaction is −18,062 cal. What is the value of $\Delta H_0{}^0$?

(*c*) Calculate ΔH^0 for the reaction at 873° K.

Ans. (*a*) $\Delta C_p = -10.54 + 0.00872T + 0.00000067T^2$.

(*b*) $\Delta H^0 = \Delta H_0{}^0 - 10.54T + 0.00436T^2 + 0.00000022T^3$.

$\Delta H_0{}^0 = -15{,}313$.

(*c*) $\Delta H^0_{873K} = -21{,}045$.

12. (*a*) Using the equation for ΔH^0 and the value of $\Delta H_0{}^0$ from the preceding problem, give an equation expressing ΔF^0 as a function of temperature. ${}^{\Delta F^0}{}_{298K} = -11{,}994$ cal. What is the value of I?

(*b*) Calculate ${}^{\Delta F^0}{}_{873K}$.

(*c*) Calculate K_p for the reaction $C_{(graphite)} + 2H_2\,(g) = CH_4\,(g)$ at 873° K from the free-energy value of (*b*).

Ans. (*a*) $\Delta F^0 = -15{,}313 + 10.54T \ln T - 0.00436T^2 - 0.00000011T^3 + IT$

$I = -47.6$.

(*b*) ${}^{\Delta F^0}{}_{873K} = 2100$.

(*c*) K_p at 873° K = 0.30.

13. Using the values of ${}^{\Delta H^0}{}_{873}$ and ${}^{\Delta F^0}{}_{873}$ obtained from Problems 11 and 12, respectively, calculate ${}^{\Delta S^0}{}_{873K}$ for the formation of methane from hydrogen and graphite. Compare the result with Problem 10*b*. *Ans.* −26.4 cal per degree.

14. From the following data show that there is a decrease of entropy in the sulfur system when monoclinic sulfur changes spontaneously into rhombic sulfur at 25°, but that there is an increase in the entropy of the surroundings which more than offsets this decrease. Thus the total entropy (of the universe) is increased, as required for a spontaneous reaction. Also calculate the free-energy change for the sulfur system, and discuss the sign. From low-temperature heat-capacity measurements the entropy of monoclinic sulfur at 25° is 7.78 cal deg^{-1} $mole^{-1}$, and that of rhombic sulfur is 7.62 cal deg^{-1} $mole^{-1}$. For the reaction $S_{monoclinic} \rightarrow S_{rhombic}$ at 25° $\Delta H = -71$ cal.

Ans. $\Delta S_{sulfur} = S_{rhombic} - S_{monoclinic} = 7.62 - 7.78$

$= -0.16$ cal $degree^{-1}$ $mole^{-1}$

$\Delta H_{sulfur} = -71$ cal = heat evolved by sulfur = heat absorbed by surroundings

$$\Delta S_{surroundings} > \frac{\text{heat absorbed by surroundings}}{T} > \frac{71}{298} > 0.24 \text{ cal/mole}$$

$$\Delta S_{total} = S_{sulfur} + S_{surroundings} > -0.16 + 0.24$$

> 0.08 cal deg^{-1} $mole^{-1} > 0$

$$\Delta F_{sulfur} = \Delta H - T\,\Delta S = -71 - 298\,(-0.16)$$

$= -71 + 48 = -23$ cal/mole

For the reaction $S_{monoclinic} \rightarrow S_{rhombic}$ the total entropy increases, and the reaction is thus spontaneous. Likewise, the free energy decreases, and, accordingly, the reaction is spontaneous.

15. Mercuric oxide dissociates according to the reaction, $2HgO = 2Hg\,(g) + O_2$. At 420° the dissociation pressure is 387 mm, and at 450° it is 810 mm. Calculate (*a*) the dissociation constants, and (*b*) the heat of dissociation per mole.

Ans. (*a*) 0.0196; 0.1794 atm. (*b*) 36,750 cal per mole.

16. At 1273° K and at a total pressure of 30 atm the equilibrium in the reaction $CO_2 + C\,(s) \rightleftharpoons 2CO$ is such that 17 molar per cent of the gas is CO_2. (*a*) What percentage would be CO_2 if the total pressure were 20 atm? (*b*) What would be the effect on the equilibrium of adding N_2 until the partial pressure of N_2 is 10 atm? (*c*) At what pressure will 25 per cent of the gas be CO_2?

Ans. (*a*) 12.5%. (*b*) No effect. (*c*) 54 atm.

17. Write the expression for the equilibrium constant K_p for the formation of nitric oxide, $N_2 + O_2 = 2NO$.

(*a*) Show that a maximum yield of nitric oxide is obtained when the nitrogen and oxygen have the same partial pressures.

(*b*) What will be the effect on K_p of compressing the equilibrium mixture so that the total pressure is increased from 1 atm to 10 atm?

(*c*) What will be the effect on the partial pressure of nitric oxide of compressing the equilibrium mixture so that the total pressure is increased from 1 atm to 10 atm?

18. (*a*) At what total pressure will PCl_5 be dissociated at 250° to the extent of 20 per cent into PCl_3 and Cl_2? $K_p = 1.78$.

(*b*) What is the weight of a liter of the partially dissociated gas at this temperature and pressure?

19. The following equation has been found to apply to the reaction $N_2O_4 \rightleftharpoons 2NO_2$:

$$\log K_p = -\frac{14{,}600}{4.576T} + 9.850$$

(*a*) Calculate the value of K_p at 50°.

(*b*) Calculate the degree of dissociation at this temperature when the total pressure is 0.5 atm.

20. Show that for a reaction of the type,

$$AB = A + B$$

at any temperature, the total pressure at which AB is 50 per cent dissociated will be numerically equal to three times the equilibrium constant K_p.

21. Adkins and Adams studied the equilibria involved in the formation of acetals by titrating the mixture and determining the aldehyde concentration. At 25°, 1 mole of ethanol was mixed with 0.091 mole of acetaldehyde in a volume of 63.0 ml, and it was found that, when equilibrium was reached, 90.72 per cent of the acetaldehyde had reacted. The reaction is

$$2C_2H_5OH + CH_3CHO = CH_3CH(OC_2H_5)_2 + H_2O$$

(*a*) Calculate the equilibrium constant, assuming an ideal solution.

(*b*) If the mixture is diluted to 300 ml with an inert solvent, what per cent of acetaldehyde will have reacted?

22. What is the free-energy change when 1 mole of N_2O_4 at 25° and 2 atm is converted into 2 moles of NO_2 at 0.2 atm? For the reaction $N_2O_4 \rightleftharpoons 2NO_2$ at 25° $K_p = 0.141$.

23. For the gaseous reaction at 200°,

$$A + 2B \rightleftharpoons AB_2$$

$\Delta F^0 = 1000$ cal. When 2 moles of B is mixed with 1 mole of A, what total pressure must be applied in order to produce a 60 per cent conversion of A into AB_2?

24. Calculate the activity of (*a*) acetone, and (*b*) ether in a solution in which ether has a mole fraction of 0.504.

(*c*) Calculate the free-energy change involved when one mole of ether is evaporated from a very large quantity of solution in which the mole fraction of ether is 0.504 and condensed in a very large quantity of solution in which the mole fraction of ether is 0.066.

25. The average molecular weights M_{avg} of NO_2 and N_2O_4 at 1 atm total pressure are given in the following table at three temperatures. The reaction is $N_2O_4 = 2NO_2$

$t°$	25°	45°	65°
M_{avg}	77.64	66.80	56.51

Calculate the degree of dissociation and the equilibrium constant at each of these temperatures.

(*a*) Plot log K against $1/T$, and determine ΔH for the dissociation of N_2O_4.

(*b*) Calculate the equilibrium constant at 35°.

(*c*) Calculate the degree of dissociation α for N_2O_4 at 35° when the total pressure is 0.5 atm.

26. The following data apply to the reaction:

$$Br_2\,(g) \rightarrow 2Br\,(g)$$

T	1123	1173	1223	1273 °K
K_p	0.000403	0.00140	0.00328	0.0071

Determine by graphical means the heat change involved when 1 mole of Br_2 dissociates completely at 1200° K.

27. In the formation of 1 mole of AgI (*s*) from solid silver and solid iodine 14,815 cal are evolved at 25°. From specific heat measurements at low temperatures the molal entropy of AgI (*s*) at 25° has been found to be 27.6 cal per degree, whereas the atomic entropy of silver at 25° is 10.2 and that of iodine is 13.3 cal per degree. Calculate the standard molal free energy of AgI (*s*) at 25°.

28. The following data for isobutene may be found in the literature. Using any that are necessary together with data of previous chapters calculate the free energy of formation of gaseous isobutene at 25° (Todd and Parks, *J. Am. Chem. Soc.*, **58**, 134 [1936]).

$S_{90K} = 10.81$ entropy units
F.P. $= -140.7°$
Heat of fusion = 25.22 cal per gram
B.P. $= -7.1°$
Heat of vaporization = 96.5 cal per gram
ΔH of formation (25°) $= -4060$ cal

Specific Heat

T	93.3	105.5	118.9	139.2	166.1	179.8	210.2	253.1°
C	0.2498	0.2749	0.3056	0.4547	0.4621	0.4681	0.4860	0.5173

29. The equilibrium pressure of solid NH_4HS is 500 mm at 25°. Assuming that the vapor is completely decomposed into NH_3 and H_2S, calculate the maximum pressure of H_2S which can be added to a system containing NH_3 at 50 mm without precipitating NH_4HS.

30. Picric acid distributes itself between the two immiscible solvents, benzene and water, at different concentrations as follows:

Conc. in Water Phase	*Conc. in Benzene Phase*
0.00208 mole/liter	0.000932 mole/liter
0.00327	0.00225
0.00701	0.0101
0.0101	0.0199

Picric acid exists as nondissociated and nonassociated $C_6H_2(NO_2)_3OH$ in benzene. What conclusions can you draw regarding dissociation or association in the water phase?

31. The heat of solution of acetic acid in water is -4180 cal and in chloroform -8778 cal. At 20° the distribution coefficient $K = c_w/c_{CHCl_3} = 14.05$. What is the distribution coefficient at 30°?

---

32. For the formation of nitric oxide $N_2 + O_2 = 2NO$ K_p at 2126.9° is 0.00251.

(*a*) In an equilibrium mixture containing 0.5 atm of nitrogen and 0.5 atm of oxygen, what is the partial pressure of nitric oxide?

(*b*) In an equilibrium mixture of N_2, O_2, NO, and other inert gases at 2126.9° and 1 atm total pressure, 80 per cent by volume of the gas is nitrogen, and 15 per cent is oxygen. What is the per cent by volume of nitric oxide?

33. When sulfur dioxide is oxidized to sulfur trioxide in the presence of a catalyst at 727° the following relation holds:

$$K_p = 1.85 = \left(\frac{p_{SO_3}}{p_{SO_2}}\right) \times \frac{1}{\sqrt{p_{O_2}}}$$

(*a*) What is the ratio of SO_3 to SO_2 when the partial pressure of oxygen at equilibrium is 0.3 atm?

(*b*) What is the ratio of SO_3 to SO_2 when the partial pressure of oxygen is 0.6 atm at equilibrium?

(*c*) What is the effect on the ratio SO_3/SO_2 when an equilibrium mixture containing 0.3 atm of oxygen is compressed so that the total pressure is doubled?

(*d*) What is the effect on the ratio SO_3/SO_2 if the total pressure of the mixture of gases is increased by forcing in nitrogen under pressure?

34. Calculate the total pressure which must be applied to a mixture of three parts of hydrogen and one part of nitrogen to give a mixture containing 10 per cent ammonia at 400°. At 400°, $K_p = 1.64 \times 10^{-4}$ for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

35. For the reaction, $N_2O_4 \rightleftharpoons 2NO_2$, K_p at 25° is 0.141. What pressure would be expected if 1 g of liquid N_2O_4 is allowed to evaporate into a liter vessel at this temperature? Assume that N_2O_4 and NO_2 are perfect gases.

36. The free energy of the reaction,

$$CO\ (g) + Cl_2\ (g) = COCl_2\ (g)$$

can be represented by the equation:

$$\Delta F^0 = -24{,}100 + 4T \ln T + 3.5T$$

Calculate the partial pressure of chlorine in equilibrium with phosgene at 200° and a total pressure of 1 atm, assuming that the gases are perfect gases.

37. Iodine and potassium iodide are known to combine to a certain extent in aqueous solution in the formation mainly of triodide. Duplicate determinations at 25° gave the following data: The concentration of KI used was 0.10000 N in the first case and 0.05019 N in the second. The sum of the concentrations of free iodine (I_2) plus the I_2 equivalent of potassium triodide was 0.008246 and 0.012687 mole per liter, respectively. The concentration of free iodine I_2 = 0.00012413, 0.000452 mole per liter, respectively. Calculate the equilibrium constant of the reaction $KI + I_2 \rightleftharpoons KI_3$.

38. The reaction,

$$2NOCl = 2NO + Cl_2$$

comes to equilibrium at 1 atm total pressure and 227° when the partial pressure of the nitrosyl chloride NOCl is 0.64 atm at 25°. Calculate ΔF^0 for this reaction, and state exactly to what process this ΔF^0 applies.

39. The reaction A (g) = B (g) is at equilibrium when A has a partial pressure of 10 atm and B has a partial pressure of 1 atm. Calculate (a) K, (b) ΔF^0; (c) calculate ΔF for the reaction:

$$A \text{ (2 atm)} = B \text{ (1 atm)}$$

Is the reaction spontaneous or not?

(d) Calculate ΔF for the reaction:

$$A \text{ (100 atm)} = B \text{ (5 atm)}$$

Is the reaction spontaneous or not?

40. Calculate the activities of the solvent ether and the solute acetone at a mole fraction of acetone of 0.20 at 30°.

41. The following reaction takes place in the presence of aluminum chloride:

$$\text{Cyclohexane} \rightleftharpoons \text{methylcyclopentane}$$

From the following data, calculate: (a) ΔF^0 at 25°, (b) ΔH at 25°:

Temperature	K_c
25°	0.143
45	0.193
65	0.272

42. From the entropy values and the heats of formation given in Chapter V, together with the value 29.1 cal degree^{-1} mole^{-1} for the entropy of Ag_2O at 25°, calculate ΔF^0 and K for the reaction,

$$2Ag_2O\ (s) = 4Ag\ (s) + O_2\ (g)$$

at 25°. What is the dissociation pressure of Ag_2O at 25°?

43. Ten grams of calcium carbonate is placed in a container of 1 liter capacity and heated to 800°. How many grams of calcium carbonate remain undecomposed? If the amount of $CaCO_3$ were 20 g, how much would remain undecomposed?

44. At 56.0° the solubility of *p*-hydroxybenzoic acid is 3.31 g per 100 g of water; at 80.0° it is 13.43 g per 100 g of water. What is the solubility at 60°?

45. The data for the solubility of urea in water are given below. Calculate the heat of solution of urea in H_2O. Up to what concentration may this solution be considered ideal? For ideal solutions the differential heat of solution is equivalent to the heat of fusion of the substance.

N_{urea}	1.000	0.9004	0.8190	0.7217	0.5680	0.4741
t^0	132.6	123.2	115.3	104.4	84.4	68.5

46. The distribution coefficient at 25° of lactic acid between water and chloroform c_{CHCl_3}/c_{H_2O} expressed in moles per liter is 0.0203. How much lactic acid will be extracted from 100 ml of a 0.8 molar solution of lactic acid in chloroform by shaking with 100 ml of water?

47. In designing a thermal diffusion tower for the separation of the isotopes of carbon in methane it is necessary to know how high the heating unit can be raised in temperature without decomposing the methane. Approximately what is the highest temperature to which methane at atmospheric pressure can be heated without decomposing more than 1.0 per cent? Thermal data can be found in Chapter VII and in Problems 10, 11, and 12.

48. Derive an equation for K_p in terms of α and P for the reaction, $2A \rightleftharpoons 2B + C$, both reactant and products being gaseous. Show that, at very large values of P and K_p, α varies inversely as the cube root of P.

49. For the reaction $2NaHCO_3 \rightleftharpoons Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(g)$, $K_p = 0.23$ at 100°. On a day when the barometric pressure was 740 mm, the room temperature 27°, and the relative humidity 0.70, 20 g of solid sodium bicarbonate was placed in a 5-liter flask and sealed with the air from the room. It was then brought up to 100°. (*a*) What was the partial pressure of CO_2 at equilibrium in the flask (if the carbon dioxide of the air is neglected)? The vapor pressure of water at 27° is 26.8 mm. (*b*) What was the pressure in the flask?

50. Estimate roughly at what temperature carbon monoxide will reduce magnesium oxide according to the reaction:

$$CO + MgO = Mg + CO_2$$

Magnesium boils at 1107°. According to thermodynamics, magnesium reacts chemically at temperatures of a few hundred degrees with oxygen, water, nitrogen, and carbon dioxide. Moreover, it reacts with carbon monoxide. Suggest possible ways in which metallic magnesium may be obtained from magnesia (MgO) and carbon. Suggest what difficulties may be encountered in the process.

51. A certain optically active organic compound slowly racemized in solution, and eventually the solution showed no optical rotation, the *d* and *l* forms being in equal concentrations. When the temperature of the solution was varied over wide limits there was no return of optical activity. What facts can be deduced about ΔF^0 and ΔH^0 for the racemization reaction?

52. Compare the equilibrium constant in gas phase and in solution for the reaction,

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$$

stating what differences, if any, exist.*

53. For the reaction $Fe_2O_3\,(s) + 3CO\,(g) \rightleftharpoons 2Fe\,(s) + 3CO_2\,(g)$ the following values of K_p are known:

$t°$ C	100	250	1000
K_p	1100	100	0.0721

At 1120° for the reaction $2CO_2\,(g) \rightleftharpoons 2CO\,(g) + O_2\,(g)$, $K_p = 1.4 \times 10^{-12}$. What equilibrium partial pressure of O_2 would have to be supplied to a vessel at 1120° containing 1 mole of solid Fe_2O_3 in order just to prevent the formation of Fe?

54. What are the possibilities of producing (*a*) methanol, (*b*) ethanol, and (*c*) hydrocyanic acid by the following reactions:

(*a*) $CO\,(g) + 2H_2\,(g) = CH_3OH\,(g)$.

(*b*) $C_2H_4\,(g) + H_2O\,(g) = C_2H_5OH\,(g)$.

(*c*) $N_2\,(g) + C_2H_2\,(g) = 2HCN\,(g)$.

Details of the thermodynamic calculations are given by Ewell in *Ind. Eng. Chem.* **32**, 147 (1940).

* Essex, *J. Am. Chem. Soc.*, **54**, 1290 (1932).

55. At 377°, $R \ln K = -16.44$ for the reaction:

$$CH_4 + 2H_2O = CO_2 + 4H_2$$

At 25° for this reaction $\Delta H^0 = 39{,}432$. Construct the equation showing the variation of ΔF^0 with temperature using specific heat data, and calculate the equilibrium constant at 500°.

56. If the heat capacities of the reactants and the products are the same in a given reaction, ΔH is independent of temperature, and log K plotted against $1/T$ gives a straight line. When they are different, the heat of reaction changes with the temperature, and the log K vs $1/T$ line is curved. Extrapolation of a straight line is much more accurate than extrapolation of a curved line. Develop some function of K which will give a straight line when plotted, so that K_p can be determined by the extrapolation of a straight line, beyond the range of the measurements.

CHAPTER XIII

PHASE DIAGRAMS

Heterogeneous Systems. A homogeneous system is one in which all parts of the system have the same physical and chemical properties. A sample from any part of the system will be the same as any other sample. Only when the samples are of about molecular size, is there any difference between them. A mixture of gases, a crystal of sodium chloride, a solution of sugar or salt in water are examples of homogeneous systems.

A heterogeneous system is a system in which the composition is not the same throughout and in which the physical properties vary in different parts. Samples may not be the same, depending on the region from which they are taken. A vessel containing water and its vapor, a mixture of benzene and water, a saturated solution containing an excess of the solute, and water with floating ice and vapor and air above it are examples of a heterogeneous system.

A phase is a definite part of a system which is homogeneous throughout and physically separated from other phases by distinct boundaries. In the examples cited, the mixture of gases is a single phase, the benzene and water system consists of two separate phases, and the water, ice, and vapor system consists of three separate phases. It does not matter whether the ice is in one large piece or in many small pieces; we are concerned only with the nature of the phases and the number of different phases.

The conditions under which these different phases can exist is a matter of considerable practical importance, and the experimental determinations of these conditions are conveniently recorded in various kinds of diagrams. It is the purpose of this chapter to describe these different types of heterogeneous systems and to show how the diagrams may be interpreted and used.

The chief variables which determine the state of equilibrium are temperature, pressure, and, in systems containing more than one independent chemical substance, the concentration of the different substances in the several phases. Time is not a variable, for the considerations apply to systems which are in equilibrium. It must be clearly understood that only relative quantities are involved and not the total

quantity of material. The same type of diagram applies whether grams or tons of material are involved.

Solubility. When a solution is in equilibrium at a definite temperature with a solid, or gas, or a second liquid, the solution is said to be *saturated*, and the concentration of the second phase in the saturated solution is known as the *solubility*. The saturated solution may be prepared by agitating the solution with an excess of the finely divided solute until there is no change in concentration on further standing. Again, the solution may be mixed with an excess of the solute at a given temperature and then changed to a temperature at which the solubility is lower. The excess solute is then thrown out, leaving a saturated solution.

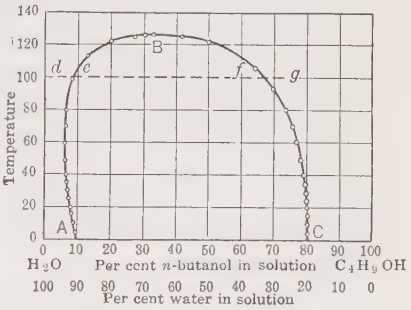


FIG. 71. Influence of temperature on the solubility of liquids, *n*-butanol and water.

Solutions of one liquid in another are discussed on page 197, but in those cases saturated solutions were not involved because the two liquids were miscible in all proportions; that is, they were entirely soluble in each other. At high temperatures water and *n*-butanol (C_4H_9OH) are miscible in all proportions, but at lower temperatures there are two separate liquids in equilibrium, one being a solution of water saturated with *n*-butanol and the other a solution of *n*-butanol saturated with water. The behavior of this system is described in **Fig. 71.**

In all regions inside the curve *ABC* there are two liquid layers, whereas outside there is but one. Temperature is plotted vertically along the *y* axis and percentage composition of the solution horizontally along the *x* axis. If one starts with a small amount of butanol and adds it in increasing quantities to a large volume of water, a concentration eventually will be reached at which the solution separates into two layers. This concentration at 0° is represented by the point *A*. When the temperature is raised, the solubility of butanol in water decreases slightly at first and then increases, as shown by the curve *AB*. In like manner, if one starts with pure butanol and adds increasing amounts of water at 0°, separation into two layers occurs at a concentration represented by the point *C*. As the temperature is raised, the solubility of water in butanol increases, as shown by the curve *CB*. When the temperature is raised above 126° corresponding to the height of the point *B*, butanol and water become soluble in all proportions.

If one starts with a solution at a temperature and composition represented by the point *d*, the addition of increasing amounts of butanol at constant temperature is represented by the dotted line *defg*. When the point *e* is reached, the solution separates into two layers. As more butanol is added, the quantity of the butanol layer saturated with water increases, but the compositions of the two layers remain constant. At *f* the solution again becomes homogeneous, and the addition of more butanol increases the concentration of butanol in the solution, as, for example, at *g*.

The solubilities of solids in liquids vary greatly with the nature of the crystal, with the solvent, and with the temperature. A saturated solution is in equilibrium with a definite crystalline solid, and, although the concentration of the saturated solution may change gradually with temperature, there is no corresponding change in the composition of the solid, except in a few cases where there is a change in crystal structure or in the number of moles of water of hydration.

The solubilities of a few typical crystals in water at different temperatures are given in **Fig. 72.** They are expressed in grams of solute per 100 g of solution, that is, in per cent by weight.

The dissolving of a solid in a liquid involves several factors. In ideal solutions the molecules break away from the crystal and fill the volume of the solvent until the solution is saturated, in the same way that molecules from a crystal fill an evacuated space. Ideal solutions are rare; usually the molecules interact with the solvent, and the mere fact that the concentration in solution is usually much greater than the concentration in a previously evacuated space indicates that the solvent is exerting a special influence on the solute.

The influence of temperature on the solubility depends on the differential heat of solution in the nearly saturated solution, as predicted by the laws of thermodynamics. Most salts absorb heat when dissolved, and, accordingly, they are more soluble at the higher temperatures, as is the case, for example, with barium hydroxide $Ba(OH)_2 \cdot 8H_2O$. A few salts are known in which the heat of solution is exothermic, and, in agreement with the thermodynamic formulas, the solubility then *decreases* as the temperature rises. When a salt exists in different hydrated forms, as is the case for sodium chromate Na_2CrO_4, the heat of solution will be different, and the temperature effect will be different. Thus, $Na_2CrO_4 \cdot 10H_2O$ has a steeper slope than $Na_2CrO_4 \cdot 4H_2O$ which, in turn, has a steeper slope than Na_2CrO_4. The higher hydrates evolve less heat when dissolved, because heat has previously been evolved when the lower hydrates were formed.

If the heat evolved by hydration of the dissolved solute nearly offsets the heat absorbed by pulling the solid crystal apart, the over-all heat of solution is nearly zero. Sodium chloride is an example of a solute which does not evolve nor absorb much heat when it dissolves in water. Thermodynamical considerations previously discussed predict that the solubility of such a solute is not changed by a change in temperature. Figure 72 shows that the solubility of sodium chloride does, indeed, remain nearly constant.

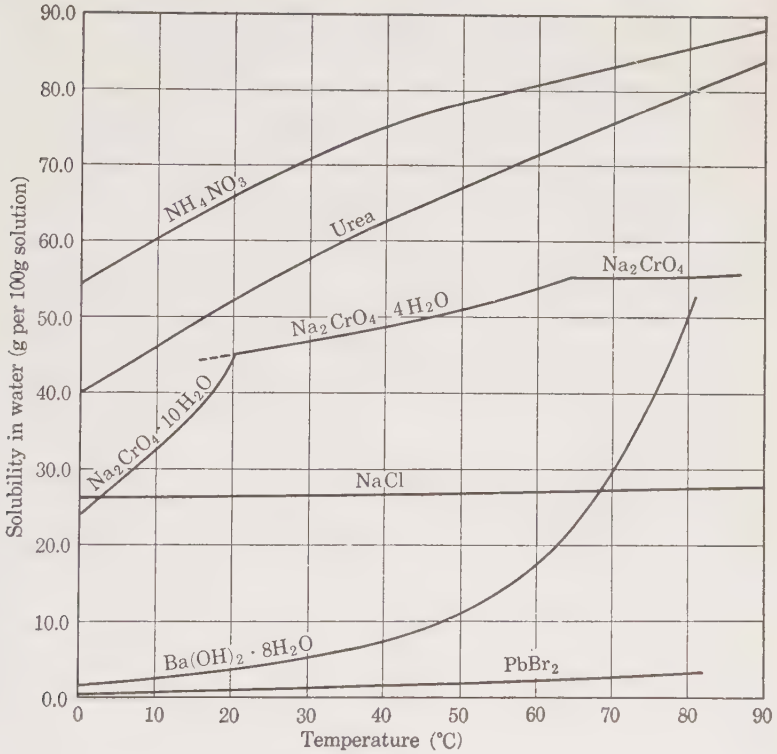


FIG. 72. Influence of temperature on the solubility of solids.

Just as an increase in temperature increases the solubility of a salt which absorbs heat, so an increase in pressure increases the solubility of a salt which dissolves with a shrinkage in volume. The influence of pressure on solubility of a solid or liquid is quite small. It is stated by van't Hoff that the solubility of ammonium chloride, which gives an increased volume on solution, decreases by 1 per cent for 160 atm, whereas the solubility of copper sulfate, which gives a decreased volume on

solution, increases by 3.2 per cent for 60 atm. These data are in agreement with the theorem of Le Chatelier and the second law of thermodynamics. Extensive work on the compressibilities of solutions has been done by Gibson.*

It is well recognized that the rate of solution of solute in a solvent is greatly accelerated by pulverizing the material so as to expose a larger area to the solvent. Quite apart from this effect, the actual equilibrium solubility of very small crystals is greater than that of large crystals.† This increase in solubility with decreasing size is not a significant factor unless the crystals are extremely small.

Supersaturated solutions are solutions which contain more than the equilibrium-saturation concentration of dissolved solute. Particularly in the case of highly soluble solutes, they can sometimes be prepared by cooling the saturated solution carefully without agitation and with special precautions to eliminate any trace of solid particles of the crystalline solute. The dotted line in Fig. 72 for $Na_2CrO_4 \cdot 4H_2O$ represents a supercooled solution of $Na_2CrO_4 \cdot 4H_2O$. Any point directly beneath this dotted line corresponds to a solution which is supersaturated with respect to $Na_2CrO_4 \cdot 10H_2O$ but unsaturated with respect to $Na_2CrO_4 \cdot 4H_2O$. A crystal of the former added to this supersaturated solution will grow in size, but a crystal of the latter will dissolve.

The explanation of supersaturation is probably to be found in the fact that the submicroscopic crystals which would normally be the first to deposit have a higher solubility, and the crystallization process cannot easily get started. When an ordinary crystal of the solute with a normal solubility is introduced, however, the extra dissolved material crystallizes out immediately. The greater solubility of the very small crystals may, perhaps, be attributed to the existence of some isolated atoms or groups of molecules which can break away from the crystal more easily. This view is strengthened by the fact that, if a mixture of large crystals and very small ones is allowed to stand, the small ones disappear, and the larger ones grow larger—a procedure which is followed in the digesting of precipitates in quantitative analysis to render them better suited for filtration.

Extremely small particles of crystals occurring, for example, as dust in a room, are sometimes sufficient to prevent supersaturation. Supersaturation can sometimes be relieved also by vibrations due to friction on glass or metal surfaces immersed in the solution.

Temperature–Pressure Phase Diagram for Water. In the preceding section the influence of temperature on solubility in a two-phase system

* Gibson, *J. Am. Chem. Soc.*, **57**, 284 (1935).

† May and Kolthoff, J. Phys. and Colloid Chem., **52**, 836 (1948).

has been described. We now turn to phase diagrams in which the influence of pressure as well as of temperature is considered and start with the interpretation of the simple and important phase diagram for water. Other phase diagrams follow throughout this chapter, increasing in complexity. The conditions of temperature and pressure under which ice, liquid water, and vapor can exist in a state of equilibrium have been

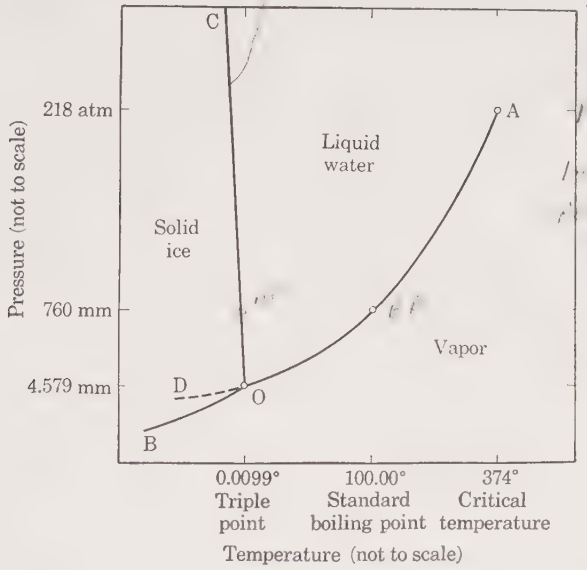


FIG. 73. Schematic pressure–temperature diagram of water showing three phases.

determined by experiment and are given in **Fig. 73** (which is not drawn to scale on account of the large range of pressures).

Three general areas are labeled in which ice, water, or vapor can exist alone. For example, vapor may exist anywhere in the area labeled "vapor," and it is necessary to specify both the pressure and the temperature in order to define the system completely. The mere statement that water vapor is present at a specified pressure does not describe the system, because the temperature variable is not defined.

Where two of these areas touch, there is a line, and along each line the two phases exist in equilibrium.

The vapor–pressure curve of water is represented by the line *OA*. Above this line liquid water exists alone; and below it water vapor exists alone. Only on the line *OA* where both regions touch is it possible to have water and its vapor in equilibrium. Thus, if the pressure is

reduced to a point below the line *OA*, all the water will be vaporized; if, on the other hand, the pressure is raised above the line *OA*, all the vapor will ultimately condense to the liquid state.

If it is stated that the system contains *both* liquid water and water vapor at 25°, it is not necessary to specify the pressure, because it has been found by experiment that water and its vapor can exist together at 25° only under a pressure of 23.7 mm. The pressure at any temperature may be read from the vapor–pressure curve. Likewise, if the pressure is stated, the temperature may be determined from the graph. A single variable, either temperature or pressure, is sufficient to describe completely the system along a line.

The line *BO* is the sublimation curve of ice. Above it lies ice, and below it lies vapor. Only along *BO* can ice and vapor exist together in equilibrium.

The line *OC* shows how the melting point changes with pressure. At all points on the line the pressure is greater than the vapor pressure, as given by the line *BOA*; so it may be concluded that no vapor is present. This line is inclined toward the vertical axis and the melting point of ice is lowered by increasing the pressure—a fact which can be predicted from the principle of Le Chatelier, since the liquid water occupies a smaller volume than the solid ice. Along *OC* there are two phases, ice and liquid water, and, again, it is necessary to specify only one variable, either temperature or pressure, to describe the system completely.

Where the three lines, representing pairs of phases, intersect, the three areas touch, and all three phases exist together in equilibrium. Only one such point is possible with three phases, and it is called a *triple point*. It is not necessary to specify either temperature or pressure under these conditions, for there is only one possible temperature and one possible pressure which will permit all three phases to exist together in equilibrium. If the temperature is raised at constant pressure, the ice will melt, and the liquid will vaporize leaving only vapor; if the temperature is lowered, there will be only ice; if the pressure on the vapor is raised at constant temperature, the vapor will condense; and, finally, if the pressure is lowered, the liquid and ice will evaporate.

Ice and water, saturated with air, are in equilibrium with their vapor in air under atmospheric pressure at a temperature of 0°. The definition of the centigrade scale depends on this fact. The situation is somewhat complicated, because the pressure of water vapor is only 4.57 mm, whereas the total pressure on the ice and water is 1 atm.

If ice and water, from which dissolved air has been removed, are allowed to evaporate into a previously evacuated space, the pressure on

the ice and water will be 4.57 mm instead of 1 atm, and the melting point will be slightly higher. The exact temperature of this triple point is 0.0099°. This difference from 0°C of 0.0099° is due to two factors. The solubility of air at atmospheric pressure is sufficient to lower the freezing point by 0.0024°, and the increase of pressure from 4.57 mm to 1 atm lowers the freezing point 0.0075°. This lowering of 0.0075° due to the pressure change checks with that calculated by the Clapeyron equation. The two effects together bring the freezing point from 0.0099° down to 0°.

The dotted curve *OD*, which is a continuation of *OA*, represents the vapor pressure of supercooled water. It may be noticed that there is no break in the vapor–pressure curve, so long as the solid phase does not separate, and that the vapor pressure of supercooled water, which is an unstable phase, is greater than that of the stable phase, ice, at the same temperature. Unstable phases always have higher vapor pressures.

The lower limit of the sublimation curve *OB* is theoretically determined by the absolute zero; the vaporization curve *OA* terminates at *A* which is the critical temperature 374°, corresponding to a pressure of 218 atm. Above this critical temperature at *A* the vapor and liquid phases become indistinguishable.

Investigations conducted by Bridgman with a view to determining the course of the fusion curve *OC* have revealed the existence of seven different crystalline modifications of ice, all of which, with the exception of ordinary ice, are denser than water. The first of these new forms of ice makes its appearance at a pressure of 2115 kg per square centimeter, and the last at a pressure of 22,400.

Temperature–Pressure Phase Diagram for Sulfur. The energy which binds the units together in a crystal lattice of a pure material has such a definite value that, when the temperature is raised gradually, a temperature is reached at which the crystal suddenly melts. At this melting point, the kinetic energy just exceeds the binding energy of the crystal. Sometimes a given element or compound can exist in two or more different crystal lattices, each of which has a different binding energy. As the temperature of such a crystal is raised, and the kinetic energy increased, the lattice which was stable at the lower temperature becomes unstable, and the crystal lattice rearranges into a form with a higher energy of binding. The *transition temperature* is the temperature at which one crystal lattice changes into another. It is a definite temperature, but the time required for the formation of a new lattice with its definite arrangement is much longer than the time required for the formation of a liquid. Accordingly, the direct determination of transi-

tion temperatures by heating or cooling is difficult and requires extended measurements over a long period of time. The transition temperature can be determined by direct observation of changes in the crystal properties, by the heat evolved in the transition, by a change in volume, or solubility, or, best, by X-ray analysis.

A diagram of sulfur, which exhibits a transition temperature, is shown in **Fig. 74.** The vertical axis is not drawn to scale because the pressures

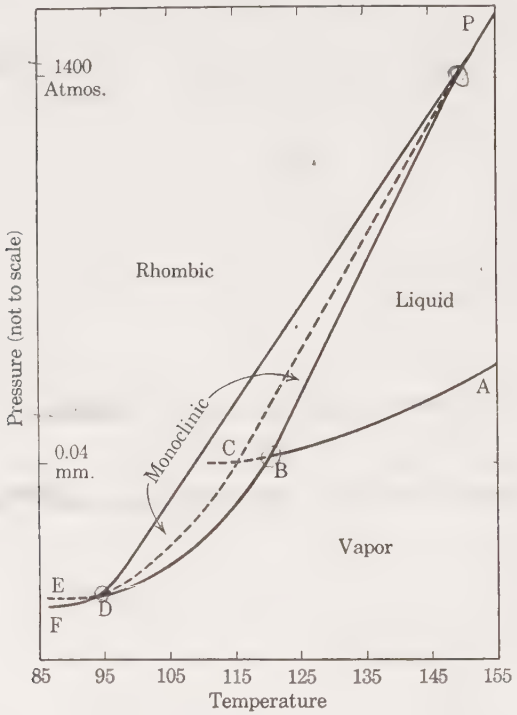


FIG. 74. Pressure–temperature diagram of sulfur which has a transition between two different crystal lattices.

cover too wide a range. It is similar to the diagram for water, each area representing a single phase, and each line an equilibrium between two phases. Whereas there were three possible phases in water, there are four in sulfur, because there are two solid phases, rhombic sulfur stable below 95.6° and monoclinic sulfur stable above 95.6°. There are more opportunities then for a group of three different phases, and we see four triple points in the sulfur diagram but only one in the water diagram.

The following phases are found at the several areas, lines, and points:

Areas

Above *FDP*	Rhombic
DBP	Monoclinic
ABP	Liquid
Below *FDBA*	Vapor

Lines

FD	Rhombic, vapor
DB	Monoclinic, vapor
DC	Superheated rhombic, vapor
BA	Liquid, vapor
CB	Supercooled liquid, vapor
BP	Monoclinic, liquid
CP	Superheated rhombic, liquid
DP	Rhombic, monoclinic
ED	Supercooled monoclinic, vapor

Points

D at 95.6°	Rhombic, monoclinic, vapor
B at 119°	Monoclinic, liquid, vapor
C at 113°	Supercooled liquid, superheated rhombic, vapor
P at 154°	Rhombic, monoclinic, liquid

The line *BP* shows that the melting point of monoclinic sulfur is raised by the application of pressure, and the liquid phase must, accordingly, have a larger volume than the solid. This is contrary to the case of the water diagram. It is known that solid sulfur sinks in liquid sulfur, whereas ice floats on water. The behavior of sulfur is typical of most solids.

It is clear that an increase in the number of phases increases the information and decreases the number of possible variables which remain undefined. The phase rule, which will be presented a little later, gives a quantitative relation between the number of phases and the number of variables.

Concentration, Temperature, and Pressure. When two or more chemical individuals are involved, the concentration of these materials as well as temperature and pressure are variables which must be specified in order to define the system completely. If there are but two substances as a salt and water, concentration may be plotted along one axis and temperature and pressure along two other axes, giving a space model

in three dimensions. Such a model is shown in **Fig. 75*a*** for the system copper sulfate and water. Temperature is plotted horizontally along the X axis, the concentration of water is plotted vertically along the Z axis,

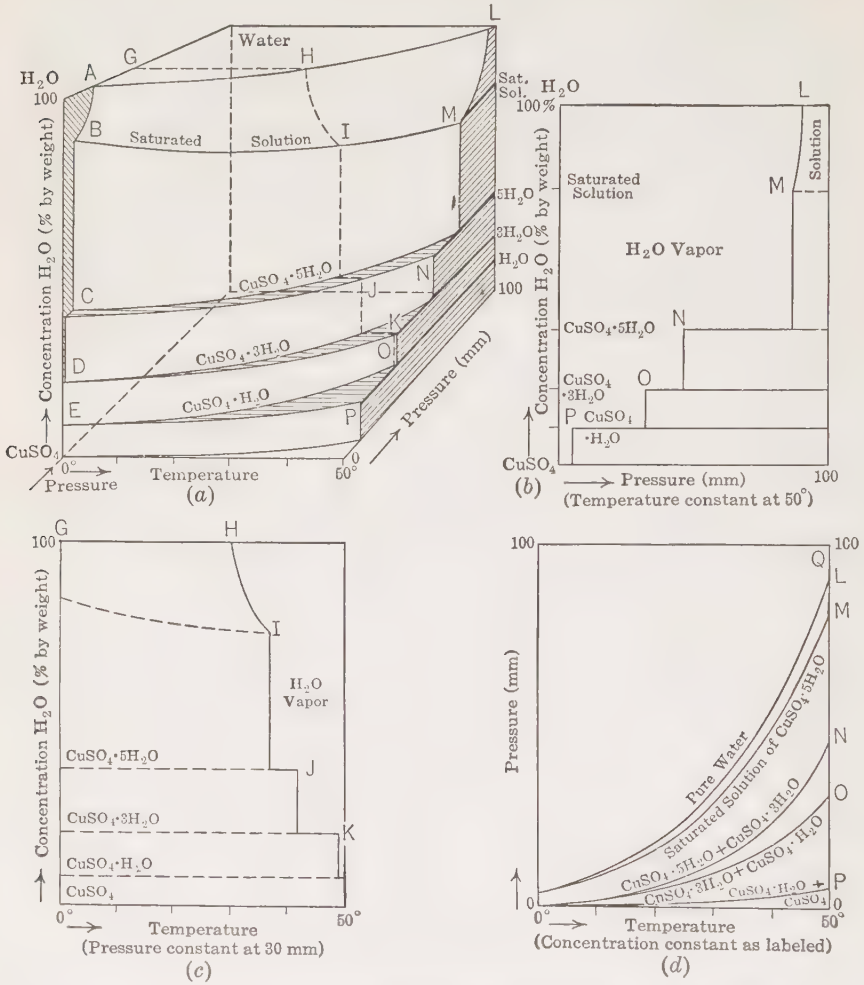


FIG. 75. Space model showing concentration, temperature, and pressure for the system copper sulfate and water.

and pressure is plotted along the Y axis at right angles to the other two. The concentrations of water corresponding to the various crystalline salt hydrates and the saturated solution are given on the concentration axis. Sections may be cut by planes at right angles to the three axes giving, respectively, a C-P diagram at constant temperature, a C-T

diagram at constant pressure, and a P–T diagram at constant concentration. In the concentration–pressure diagram of **Fig. 75*b*,** curves are given at a temperature of 50°. The concentration–temperature relations at a constant pressure of 30 mm are shown in **Fig. 75*c*.** In the pressure–temperature diagram, shown in **Fig. 75*d*,** the intersections of the space model by horizontal planes are given for concentrations corresponding to each of the salt hydrates and the saturated solution. The lines in Fig. 75*d* may be regarded as projections onto the basal plane. Water vapor exists in the region in front of the space model. Only condensed phases, salt hydrates, and solution exist inside of it.

The C–P diagram, shown in Fig. 75*b*, illustrates the behavior of a solution of copper sulfate when it is placed, with an excess of dehydrating agent, in a desiccator at 50° provided with a manometer and allowed to lose water gradually until only the anhydrous salt remains.

As water is removed from the solution the concentration of copper sulfate increases, and the vapor pressure of the solution decreases along the line LM. When the solution becomes saturated, the pressure remains constant, as shown by the vertical line at M, while the water is removed from the saturated solution. The composition of the whole system changes as water is removed.

The relative amounts of saturated solution and $CuSO_4 \cdot 5H_2O$ change, but the composition of the two phases does not change; hence, the vapor pressure remains constant. Finally, when all the solution has disappeared, the pressure drops abruptly to 47 mm at N. The pressure over completely hydrated copper sulfate remains constant at 47 mm, until the salt has been deprived of 2 moles of water, when it drops abruptly to 30 mm at 0 and remains constant until 2 more moles of water have been lost at P. It then drops to 4.5 mm, and remains constant until dehydration is complete. In practice, the lines are less steep because of slow diffusing of the water vapor.

The constant pressures correspond to systems in which there are two phases in addition to the vapor phase—all in equilibrium with each other. Unsaturated solutions of varying concentrations at the right of M in Fig. 75*b* have only two phases, one liquid and one vapor. Accordingly, they can have different vapor pressures at the specified temperature (50°). However, as soon as the solid phase $CuSO_4 \cdot 5H_2O$ crystallizes out, the composition of the two phases becomes fixed, and the vapor pressure remains constant. After all the water has been removed from the solutions, the $CuSO_4 \cdot 5H_2O$ starts to lose water and immediately forms $CuSO_4 \cdot 3H_2O$. These two hydrated salts then set up a new equilibrium

and a new fixed vapor pressure. The several equilibria are as follows:

$$\text{Saturated solution} \rightleftarrows CuSO_4 \cdot 5H_2O + H_2O$$

$$CuSO_4 \cdot 5H_2O \rightleftarrows CuSO_4 \cdot 3H_2O + 2H_2O$$

$$CuSO_4 \cdot 3H_2O \rightleftarrows CuSO_4 \cdot H_2O + 2H_2O$$

$$CuSO_4 \cdot H_2O \rightleftarrows CuSO_4 + H_2O$$

Since the pressures of the solids $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 3H_2O$ are constant, an equilibrium constant can be written, thus,

$$K_p = p_{H_2O}{}^2$$

and similar equilibrium constants can be written for the other reactions. The vapor pressure is constant only when an equilibrium exists, and an equilibrium can exist only when two hydrated salts and water vapor are present together.

Mixtures of two different crystalline salt hydrates are useful in establishing definite partial pressures of water. There are many different hydrated salts to choose from, so that it is possible to obtain nearly any desired pressure. Sometimes the partial pressures of the anhydrous salt and the lowest hydrate are so low that they are used for dehydrating agents. Zinc chloride or calcium chloride is suitable. At 25° the mixture of $CuSO_4 \cdot H_2O$ and $CuSO_4$ has a partial pressure of 0.8 mm of water, and, accordingly, anhydrous copper sulfate will not take up any water at this temperature if the vapor pressure is less than 0.8 mm.

Of the three possible relations, *C–P*, *C–T*, and *P–T*, the temperature–concentration diagrams are most frequently used.

These diagrams can be studied best with the help of the phase rule now to be discussed.

The Phase Rule. In 1876 Professor J. Willard Gibbs * of Yale University discovered a generalization known as the phase rule † which has been of great help in studying equilibria in heterogeneous systems. The phase rule, together with his many important generalizations in thermodynamics, has given Gibbs a position as one of the geniuses of science. Phase diagrams and the phase rule have been of great value in solving practical problems such as the preparation of alloys or salts from complicated mixtures and the adjustment of temperature, pressure, and composition to obtain a desired product. The extraction of potassium chloride from the Stassfurt salt deposits was one of the early examples.

* Gibbs, *Trans. Conn. Acad. Sci.*, 1876–78.

† A brief derivation may be found in Findlay and Campbell "The Phase Rule and Its Applications," Longmans, Green & Co., New York, 1938.

It should be pointed out that the phase rule applies only to systems which are in a state of equilibrium, that it does not predict new things, but that it is very valuable in correlating data. It may be used to state what type of relations may be expected, but the exact shape of the curves relating different variables must be determined by experiment.

In general, the phase rule is concerned with the *number* of variables which are involved in any system and with the *number* of relations between these variables. The ordinary variables are temperature and pressure and the concentration of materials in each of the phases. The fundamental statement of the phase rule is

$$F = C - P + 2 \tag{1}$$

where F is the number of degrees of freedom, C is the number of the components, and P is the number of phases. These terms need further definition.

A phase has been defined before as a homogeneous region of uniform physical and chemical composition. In a system containing ice, liquid water, and water vapor in equilibrium there are three phases. It makes no difference how many pieces of ice are floating on the water; there is just one ice phase.

The number of components C is the minimum number of chemical constituents which must be specified in order to describe the composition of each phase present. In the system $CaCO_3$ $(s) \rightleftharpoons CaO$ $(s) + CO_2$ (g) there are three chemical individuals, but the number of components is only two because the three constituents are connected by an equilibrium. The simplest choice of components is CaO and CO_2, but $CaCO_3$ and CO_2, or $CaCO_3$ and CaO, could be chosen; in the latter case the composition of the CO_2 phase could be obtained by taking the difference between the $CaCO_3$ and the CaO. In the system ice, water, and vapor, previously referred to, there is one component, H_2O. At very high temperatures there would be some oxygen and some hydrogen in equilibrium, but at ordinary temperatures this dissociation is neglected.

The number of degrees of freedom F is the number of independent variables, temperature, pressure, and concentration in the different phases, which must be specified in order to define the system completely. A mere change in the relative amounts of the phases present is not considered as a variable. Another definition of F is the number of variables which may be changed independently without causing the appearance or disappearance of a phase.

The greater the number of chemical substances present, the greater is the number of variables. On the other hand, the greater the number of phases, the fewer is the number of variables. The presence of several

phases gives added information about the system and reduces the number of independent variables which must be defined, that is, the number of degrees of freedom. The phase rule simply gives the quantitative relation between the variables $F = C - P + 2$. The number 2 is valid only if there are two variables, commonly temperature and pressure, in addition to concentration. If there is a third variable such, for example, as a magnetic field, the phase rule becomes $F = C - P + 3$. Again, if the conditions are so fixed that the pressure is not a variable, and there is only one variable in addition to concentration, then,

$$F = C - P + 1 \tag{2}$$

Referring now to the one component system water shown in Fig. 73, we remember that in the areas two variables, temperature and pressure, had to be stated in order to define the system completely. Here $F = 2$, because $C = 1$ and $P = 1$ and $F = C - P + 2 = 1 - 1 + 2 = 2$. Along any of the lines, if one variable is specified, it was shown that the condition of the system is completely defined. There are two phases along a line. Then $F = C - P + 2 = 1 - 2 + 2 = 1$. At the point O there are three phases, and so $F = C - P + 2 = 1 - 3 + 2 = 0$. It was shown that at this point the conditions are completely fixed. Neither temperature nor pressure can be altered without losing one of the the three phases; that is, there are no degrees of freedom.

Two-Component Systems. In two-component systems Table I summarizes the phase-rule relations.

TABLE I

PHASE RULE RELATIONS FOR A TWO-COMPONENT SYSTEM

Number of Phases	Possible Variables	Number of Variables	Number of Degrees of Freedom $F = C - P + 2$	Relations Which May Be Deduced
1	p, T, X_A^{I}	3	3	All the variables are independent.
2	p, T, X_A^{I}, X_A^{II}	4	2	Two independent variables.
3	p, T, X_A^{I}, X_A^{II}, X_A^{III}	5	1	Only one variable may be chosen independently.
4	p, T, X_A^{I}, X_A^{II}, X_A^{III}, X_A^{IV}	6	0	All variables are fixed.

The subscripts refer to the component and the superscripts to the phase. Thus X_A^{H} signifies the concentration of A in the phase H. Inasmuch as the maximum number of independent variables is three, the system may be represented by a space model as in Fig. 75 for the system $CuSO_4$ and H_2O.

Since three-dimensional models of this type are difficult to construct and use, the two-dimensional graphs representing sections of the space model are usually employed. The significance of these sections was il-

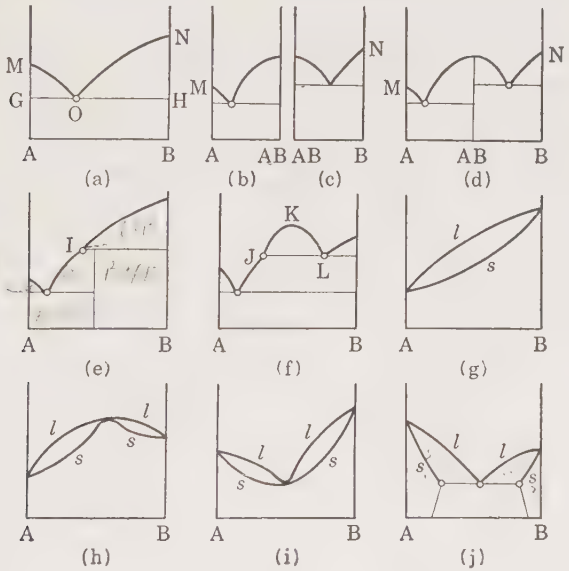


FIG. 76. Typical concentration–temperature phase diagrams.

lustrated in Fig. 75. Of the three possible planes, P–C, P–T, and T–C, the temperature–composition (T–C) diagrams are much the most common. Several important types of two component systems are illustrated in **Fig. 76** in which temperature is plotted vertically and composition horizontally; A represents 100 per cent of one component, and B represents 100 per cent of the other. The composition is given in per cent by weight, or, more significantly, in mole per cent or mole fractions. The space above the uppermost lines represents liquid solution, and along these lines a new solid phase or phases separate. The fixed pressure is taken high enough to condense all the vapor so that the diagrams refer to condensed systems containing only solid and liquid phases. Then, by the phase rule,

$$F = C - P + 1$$

In Fig. 76*a* the freezing point of pure A is shown at M. Along the line MO pure solid A is separating out from the solution. The point N represents the freezing point of pure B, and along the line NO pure solid B is separating. At O both pure solid A and pure solid B appear together. This is known as the *eutectic temperature.*

The phase rule is powerless to predict the curves MO and NO or the position of O. They must be determined by experiment. The phase rule, however, shows that, in the area above MON, temperature and composition may be varied without the number of phases being changed, because $F = C - P + 1^* = 2 - 1 + 1 = 2$. Along MO or NO, fixing either the temperature or the composition of the solution defines the system. Then, $F = 2 - 2 + 1 = 1$.

At the point O, $F = 2 - 3 + 1 = 0$ and, if any change is made in concentration or temperature, one of the two solid phases or the liquid phase will disappear. In the area $AGHB$, there are the two solid phases A and B. In the area GOM, there are two phases, solid A and liquid solution, whereas, in HON, there is solid B and liquid solution.

Figures 76*b* and *c* help to explain Fig. 76*d*. Figure 76*b* is just like Fig. 76*a* except that a compound of A and B, namely, AB, takes the place of B. The freezing point of AB is lowered by adding A to the solution. The pure solid AB separates when the solution is cooled. Figure 76*c* is similar to Fig. 76*a*, except that AB takes the place of A and its freezing point is lowered by additions of B. When these two parts, *b* and *c*, are pushed together, we have Fig. 76*d* which is typical of two-component systems in which a compound is formed. In general, a maximum in a temperature–composition curve, in which solids separate from the liquid phase on cooling, indicates the formation of a chemical compound, and the composition at which this maximum occurs is the composition of the solid compound. It corresponds to a stoichiometric ratio such as AB, AB_2, AB_3, A_2B_5, etc. In studying a system of this kind, it is best to draw vertical lines down from the maximum as shown and consider the diagram as two separate diagrams as in Figs. 76*b* and *c*. If the compound dissociates extensively in solution, the maximum is rather flat on top, and, if it dissociates but slightly, the approaches to the maximum are steep.

Figure 76*e* illustrates a special case of compound formation in which the freezing point of one of the components is so far above that of the compound that its freezing-point curve intersects the freezing-point curve of the compound on the opposite side of the maximum. The maximum can be attained only under condition of unstable equilibrium. Above the break at I, pure B separates on cooling and below it the com-

* The pressure is fixed.

pound AB separates. Such a point I is sometimes called an incongruent melting point.

Figure 76*f* illustrates the case in which two *liquid* phases are involved. The freezing point of A is lowered by the addition of B, and the freezing point of B is lowered by the addition of A, as shown at the extreme ends of the diagram. Along the line JK, the liquid phase consists of A saturated with B, and, along the line KL, the liquid phase consists of B saturated with A; these two saturated phases do not mix with each other. The point K does not correspond to any particular compound or ratio. At temperatures above K, only one liquid phase is possible, no matter what the composition. In the area JKL, two liquid phases exist.

The remaining Figs. 76 *g–j* apply to two component systems in which the two solids are soluble in each other. They are discussed in a later section. The solid separating on cooling is not a pure substance but a solution of one substance in the other, the exact composition of the separating phase depending on that in the liquid phase. In Figs. 76*g*, *h*, and *i* there is complete solubility of the solid phases, but in Fig. 76*j* the solubility is limited so that two different solid solutions giving two separate phases can exist side by side.

Cooling Curves. Cooling curves may be used in the method of thermal analysis to construct phase diagrams. It is convenient, particularly for alloys where the chemical analysis of the separating phases is difficult on account of the contaminating liquid. A mixture of known composition is weighed out and heated until all is liquefied. Then it is allowed to cool, and the temperature is recorded at frequent intervals as read on a thermometer or thermocouple. A smooth cooling curve is plotted from the data, but, whenever a solid phase separates, heat equivalent to the heat of fusion is evolved and offsets fully or in part the heat lost from the melted material and container. The rate of cooling, that is, the slope of the line, becomes less, and the temperature at which an inflection point or plateau occurs can be used in plotting the phase diagram.

This method is illustrated in **Fig. 77** for the bismuth–cadmium system. The cooling curve for pure bismuth indicated by 0 per cent cadmium is shown at the extreme left. The liquid cools off along AB, but, when B is reached, solid bismuth appears, and the temperature remains stationary at 273° until all the liquid has solidified. The cooling curve of the solid bismuth is shown along the line BC. A similar curve for the freezing point of pure cadmium is indicated by the line marked 100 per cent cadmium, which indicates a freezing point at 323°. The line marked 40 per cent shows a single plateau D which corresponds to the

eutectic point at 140°, where both solid bismuth and solid cadmium are coming out together and evolving heat. Other compositions show two changes in curvature, a sharp plateau at the eutectic point, and a more gradual nick in the curve at a higher temperature. In the mixture containing 20 per cent cadmium, pure bismuth starts to solidify from the solution at E. As it does so, the remaining solution becomes more con-

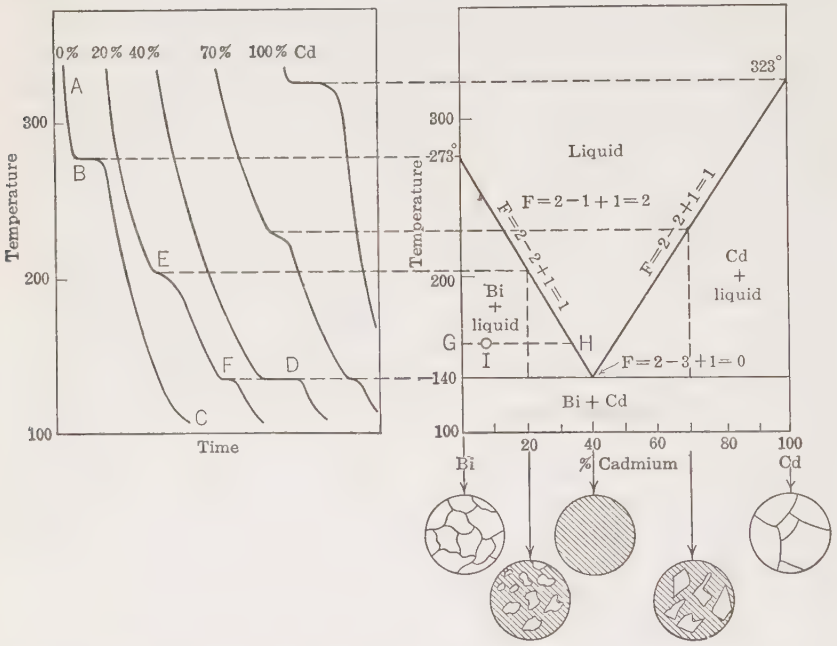


Fig. 77. Cooling curves from which temperature–concentration phase diagram is constructed for the system bismuth and cadmium.

centrated in cadmium, and the freezing point is lowered gradually as the composition changes. Finally, at F solid cadmium as well as solid bismuth separates out, and the whole system goes solid. The system consists of 80 per cent solid bismuth and 20 per cent solid cadmium, just as the original liquid system consisted of 80 per cent and 20 per cent of the liquids.

These freezing points and the eutectic point are then transferred, as shown by dotted horizontal lines, to the diagram at the right in which the temperatures are plotted against the compositions of the corresponding mixtures.

The System Bismuth–Cadmium. In the phase diagram shown at the right of Fig. 77, temperature and composition are the only variables;

the pressure is assumed to be fixed and at a value high enough so that all the vapor is condensed, giving only solid and liquid phases. Then $F = C - P + 1 = 2 - P + 1$. The number of components, phases, and degrees of freedom are marked at significant areas, lines, and points.

Below the eutectic point the two solids, bismuth and cadmium, are present. In this region there are two components and two phases, pure bismuth and pure cadmium, so that $F = 2 - 2 + 1 = 1$. The composition of each phase is known, and the only variable is the temperature which gives the one degree of freedom to the system. As explained before, the pressure is fixed, and the vapor phase is considered negligible. In any mixture, cooled below the eutectic temperature, the solid which separates will have crystals of both bismuth and cadmium. When the eutectic mixture solidifies, the solid may appear to be different because it is fine-grained, but it is not to be regarded as a new phase. It is still a physical mixture of *two* phases, solid bismuth and solid cadmium. The different solidified mixtures would have an appearance under the microscope somewhat similar to that indicated in the circles.

In the region labeled Bi + liquid there are two separate phases, solid bismuth, and liquid solution. There is one degree of freedom ($F = 2 - 2 + 1 = 1$) and the system is completely defined as soon as the temperature or the composition of the liquid phase is specified. As one passes along a horizontal line (that is, isothermal), *GIH*, the ratio of solution of composition *H* to pure solid bismuth, gradually increases. At the point *I*, for example, the ratio of bismuth to liquid of composition *H* is equal to *IH/IG*. The composition of the liquid does not change, however, and, along the line *GIH*, $F = 0$ because the temperature as well as the pressure is fixed. The composition of the total system will change as the relative amounts of *G* and *H* change, but the amounts of material in the total system does not constitute a phase-rule variable. It is the concentration of material in a given phase that is significant.

Systems Exhibiting Chemical Interaction. As pointed out in connection with Fig. 76*d*, the presence of a maximum in a freezing-point–composition curve indicates the existence of a chemical compound between the two components. In the temperature–concentration diagram given in **Fig. 78,** a maximum is shown in the liquid–solid curve, and so it may be concluded that the zinc and magnesium interact to give a chemical compound. The compound has the formula $MgZn_2$, and it melts at 575°. There is one eutectic point at 368° with Zn and $MgZn_2$ separating out together and another at 347° with Mg and $MgZn_2$ freezing simultaneously. The diagram is split into two by passing a vertical line through the maximum, and the same conditions apply that applied to Fig. 77 and Fig. 76*d*. The pressure is fixed, and only solid and liquid

phases are represented. It is assumed that the pressure is high enough to condense all the vapor.

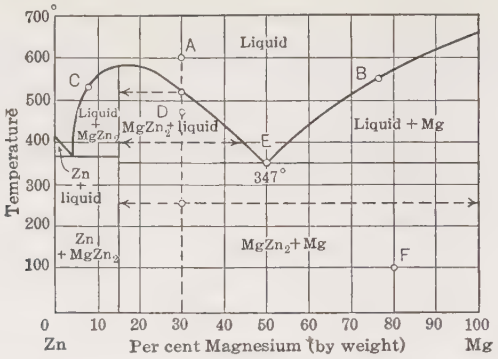


FIG. 78. Temperature–concentration phase diagram showing maximum for the system zinc–magnesium.

Example 1. State what phases are present at *A*, *B*, *C*, *D*, *E*, and *F*, and give the number of degrees of freedom. There are two components and the pressure is fixed.

	Phases	Degrees of Freedom
		$C - P + 1 = F$
A	Liquid	$2 - 1 + 1 = 2$
B	Liquid, solid Mg	$2 - 2 + 1 = 1$
C	Liquid, solid $MgZn_2$	$2 - 2 + 1 = 1$
D	Liquid, solid $MgZn_2$	$2 - 2 + 1 = 1$
E	$MgZn_2$, liquid, Mg	$2 - 3 + 1 = 0$
F	$MgZn_2$, Mg	$2 - 2 + 1 = 1$

In the region *D*, it is sufficient to fix either temperature or concentration of the liquid phase. The ratio of $MgZn_2$ to liquid is not a variable, because the concentration *in the phases* is all that counts in the phase rule, and this is fixed when either temperature or composition of a phase is fixed.

Example 2. Seventy grams of zinc and 30 g of magnesium are heated to 600° giving the point *A* in Fig. 78. Describe what happens when this total mixture is cooled down to 0°, as indicated by the vertical dotted line. (The experiment would have to be done in an inert atmosphere to prevent oxidation by air.) At 520° solid $MgZn_2$ separates out, as indicated by the top arrow; the remaining solution becomes richer in the solute magnesium; the temperature falls still lower; and more solid $MgZn_2$ is thrown out of solution. The freezing point is gradually lowered as the solution becomes richer in Mg. At 400° a considerable amount of $MgZn_2$ has come out of solution, leaving a solution of 42 per cent magnesium and 58 per cent zinc, as indicated by the arrows. Finally, at 347°, when the liquid has become 49 per cent magnesium and 51 per

cent zinc, the whole solution freezes, solid $MgZn_2$ and solid Mg coming out together.

From this temperature down to 0° there is no further change in composition or phases. At all temperatures below 347° there are pure solids Mg and $MgZn_2$. The ratio of the amounts of the two is $MgZn_2/Mg = (100 - 30)/(30 - 15) = 4.67$.

Phase diagrams are useful in the study of aqueous solutions as well as metallic solutions. Many of these solutions form definite hydrates and

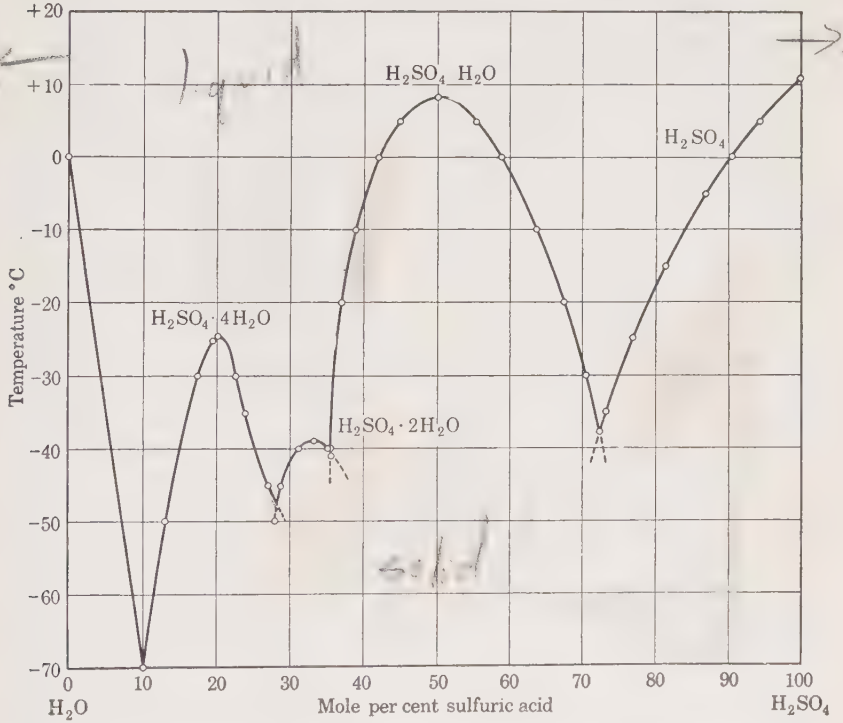


FIG. 79. Temperature–composition phase diagram for the system sulfuric acid–water.

exhibit maxima similar to those shown in Fig. 76*d* and in Fig. 78 for Zn–Mg. An example is shown in **Fig. 79** for solutions of sulfuric acid in water.

When sulfuric acid is added to water, the freezing point is lowered, as shown by the line along which there is an equilibrium between solid ice and the liquid solution of sulfuric acid in water. This lowering continues until at about 10 mole per cent of sulfuric acid the freezing temperature is about −70°. Further addition of sulfuric acid to the solu-

tion now leads to the precipitation of a new solid phase $H_2SO_4 \cdot 4H_2O$. At the first eutectic there are two solid phases, ice and $H_2SO_4 \cdot 4H_2O$, and one liquid phase (10 mole per cent sulfuric acid), so that

$$F = C - P + 1 = 2 - 3 + 1 = 0$$

This point is a eutectic point, but in aqueous solutions a eutectic point is called a cryohydric point, and the eutectic mixture is called a cryohydrate. When first discovered, these cryohydrate mixtures were thought to be chemical compounds, but the lack of homogeneity can be detected under the microscope. Furthermore, the constituents are seldom present in simple whole-number ratios which correspond to chemical compounds.

When there are exactly 4 moles of water to 1 of sulfuric acid, the solution freezes sharply at the freezing point of this pure compound. Addition of more sulfuric acid to the solution lowers the freezing point along the line leading to a second eutectic point.

In a similar manner, it is found that there are three compounds of sulfuric acid and water and four cryohydrates or eutectic mixtures.

The chemical compound $H_2SO_4 \cdot H_2O$ melts at 8.0° above the freezing point of water. It is interesting to consider what happens when water is removed (by evaporation) from dilute sulfuric acid, isothermally at 0°. The remaining solution becomes more concentrated in sulfuric acid through loss of water, and the concentration moves along a horizontal line to the right until the solubility curve is intersected and crystals are formed. The solution gradually solidifies, but on further removal of water another solubility curve is intersected, and the crystals disappear. This alternate crystallization and melting by removal of water vapor would have been difficult to understand without the phase diagram. Diagrams of this type are of great practical importance for obtaining specified products or properties through the control of concentration and temperature.

Solid Solutions. In aqueous solutions and in most common solutions in the laboratory the solvent freezes out as a pure solid. However, there are many solutions in which the solid solvent which freezes out contains the solid solute dissolved in it. An example is a solution of iodine dissolved in benzene. When the temperature is lowered to about 5°, the crystals of benzene which freeze out are colored with iodine, and the amount of iodine dissolved in the solid is proportional to the amount of iodine dissolved in the liquid solution. There is a distribution of iodine between the liquid and solid phases, just as there is distribution between two immiscible solvents. A homogeneous mixture of two or more crystalline solids in varying proportions is known as a *solid solution*.

The attainment of equilibrium in solid solutions is much slower than the attainment of equilibrium in liquid solutions. It takes a considerable length of time, particularly at low temperatures, for a change in concentration at the surface to affect the concentration at a point in the interior of the solid solution. Slow diffusion does take place, however. For example, when a bar of gold and a bar of lead were placed in contact at room temperature for a period of four years, gold was detected at a distance of 7 mm. The way is open now to study diffusions of this type

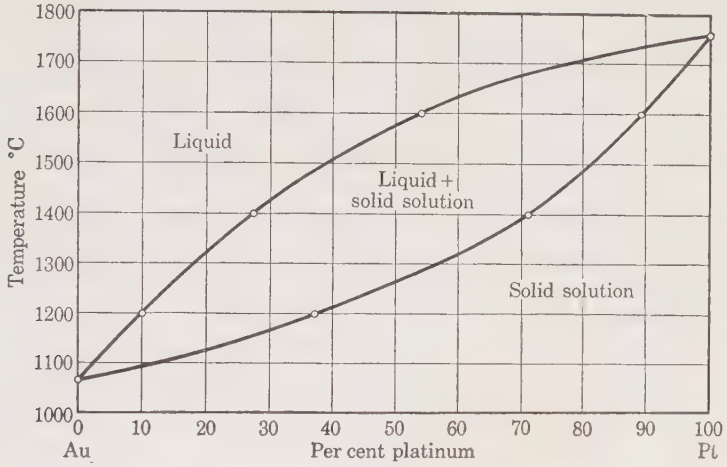


FIG. 80. Temperature–concentration phase diagram for solid solutions, platinum–gold.

with the merest trace of material, making use of radioactive tracers (page 663).

The existence of these solid solutions causes difficulty in experimental measurements of equilibria, and it introduces complications in phase-rule diagrams, as is indicated in Figs. 76*g–j*.

Solid solutions involve *two* solutions, one liquid and one solid, in equilibrium with each other, as shown, for example, in **Fig. 80** for platinum and gold. Above the upper line the two metals exist in liquid solutions; below the lower line the two metals exist in solid solutions. The upper curve is the freezing-point curve, and the lower one is the melting-point curve. The space between the two curves represents *mixtures* of the two solutions—one liquid and one solid solution in equilibrium. For example, a mixture which originally contained 50 per cent gold and 50 per cent platinum, when brought to equilibrium at 1400°, will consist of two phases, a solid phase containing 70 per cent platinum and a liquid phase containing 28 per cent platinum. If the original mixture contained

60 per cent platinum, there would still be the same two phases containing 28 and 70 per cent platinum, but there would be a relatively greater amount of the solid phase containing 70 per cent platinum.

The diagrams which describe the melting behavior of solid solutions are quite like those studied earlier which described the vaporization of liquids. For the vaporization curves it was helpful to remember that at a given temperature the vapor is richer in the more volatile component or mixture. In these solid solutions, it is convenient to remember that the liquid phase is richer in that component or mixture which has the lower melting point. In this way one can determine which is the liquid curve and which is the solid curve.

It is possible to separate materials which form an unbroken series of solid solutions by fractional crystallization just as it was shown to be possible, in Fig. 54 on page 207, to separate two compounds by fractional distillation. For example, if it is desired to separate pure gold from an alloy containing 70 per cent platinum, the alloy is melted slightly to give a liquid richer in gold, which is removed and then frozen completely. It is then melted partially to give liquid still richer in gold, and so on until pure gold is obtained.

The fractional crystallization of solid solutions is seriously complicated by the fact that equilibrium is reached very slowly, and it is often impractical to wait long enough to obtain the separations previously predicted on the basis of reaching equilibrium at every stage.

Solid solutions may contain minima in the freezing-point curves analogous to the vaporization curves on page 209 which had a minimum boiling point. An example is given for cobalt and chromium shown in **Fig. 81.** Again the liquid or mixture with the lowest melting point is in excess in the liquid phase. In this case it is the mixture of 46 per cent chromium melting at 1320° which has the lowest melting point. There are two sets of solid solutions with different properties, the α solid solutions with less than 46 per cent chromium and the β solid solutions with more than 46 per cent chromium. It is theoretically possible to separate pure chromium from solutions having more than 46 per cent chromium and pure cobalt from solutions having less than 46 per cent chromium, but it is not possible to separate pure chromium starting with a solution rich in cobalt.

Partial Miscibility. Sometimes two different liquids or two different solid solutions are miscible only within certain temperature ranges and immiscible within other temperature ranges. The phase diagrams then become somewhat more complicated.

If we consider the separation of partially miscible liquids by vaporization, **Fig. 82,** for water and *n*-butanol serves as an illustration.* The

* Stockhardt and Hull, *Ind. Eng. Chem.*, **23,** 1438 (1931).

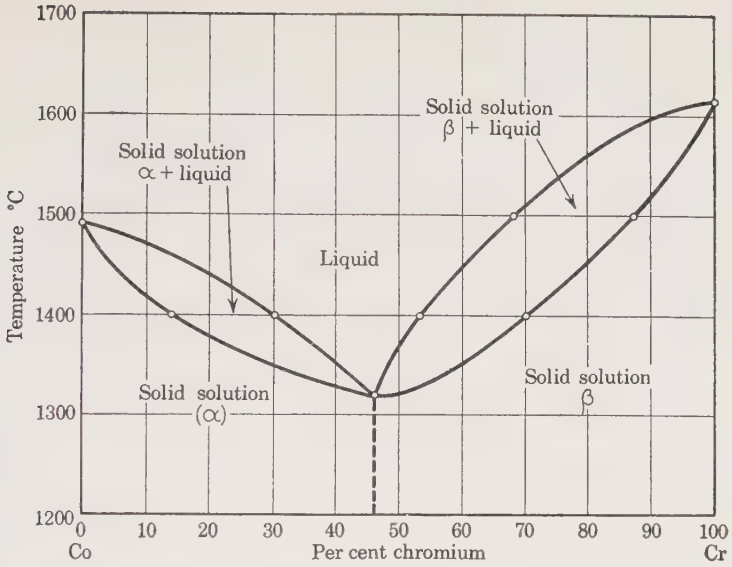


FIG. 81. Temperature–concentration phase diagram for solid solution exhibiting a minimum, cobalt–chromium.

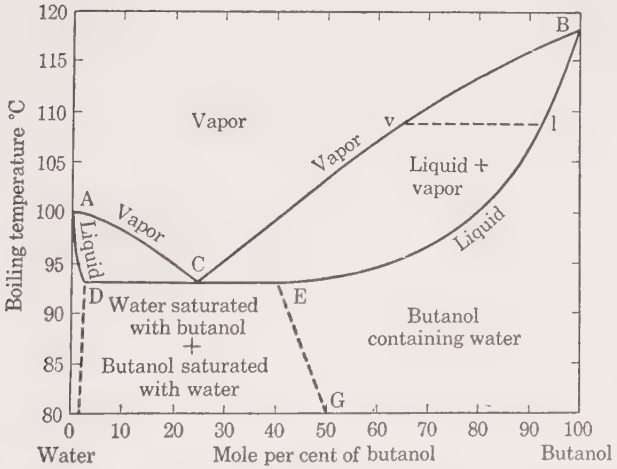


FIG. 82. Temperature–concentration phase diagram for partially miscible liquids and vapor.

lines AC, AD, BC, and BE give a diagram like that of Fig. 56 on page 209 for a pair of liquids which exhibit a minimum boiling point, but it is cut off by a straight line at about 94°.

If a solution of composition l is evaporated, the vapor will contain more water than the solution, the solution will become richer in n-butanol, and the temperature will rise until the boiling point of pure butanol is reached. If, however, a mixture lying between D and E is evap-

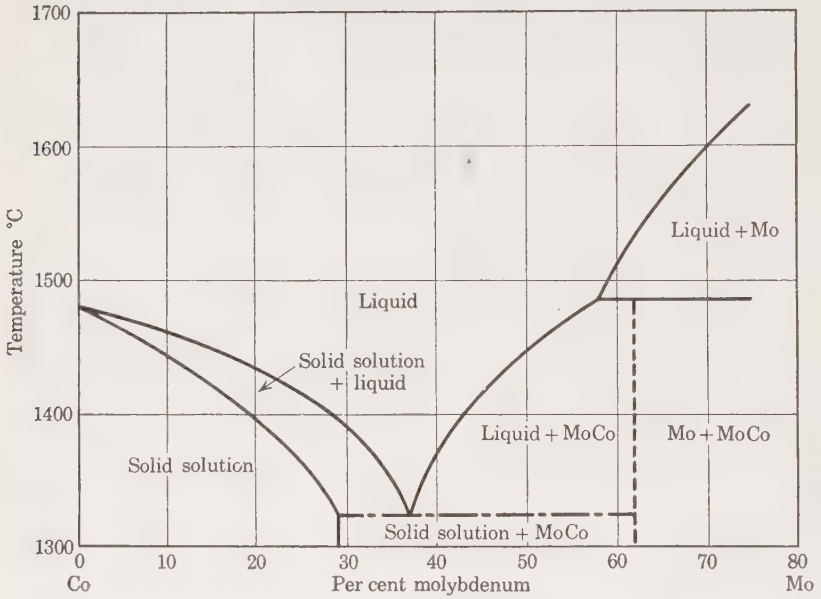


Fig. 83. Temperature–concentration phase diagram for partially miscible solid solutions, molybdenum–cobalt.

orated, the boiling point remains constant as long as the two phases are present. One is of composition D which is rich in water and the other of composition E which is less rich in water. The composition of each phase remains unchanged when the mixture of the two solutions is evaporated as long as both phases are present, but the relative amounts of the phases change. The composition of the vapor is given by C, and it remains constant until one of the phases is evaporated away. If only the butanol-rich phase remains, the temperature will rise along the line EB, and the composition of the vapor at any liquid composition can be determined by drawing a horizontal line similar to lv.

The range of compositions of water and n-butanol in which there are two phases below 94° is shown in Fig. 71 on page 305. (It is to be noted

that Fig. 71 is plotted in weight per cent and Fig. 82 in mole per cent.) At lower temperatures, as, for example, when distilling under reduced pressure, the range of immiscibility is wider, and so the line *DE* of constant composition and boiling temperature would broaden along the dotted lines *EG* and below *D*.

In **Fig. 83** is shown the system molybdenum and cobalt which bears a resemblance to the partially miscible liquids of Fig. 82 and the solid solutions of Fig. 80. Solid solutions are observed, but solid solutions with more than 29 per cent molybdenum do not mix with the cobalt–molybdenum compound. From this diagram it is possible to predict what products will be obtained by fractional crystallization, starting with various composition and temperature ranges.

Figure 83 exhibits another phenomenon in phase diagrams shown in Fig. 76*e*. Under equilibrium conditions the freezing-point curve for the Co·Mo compound does not reach the maximum temperature, the melting point of the pure Co·Mo, because it is intersected first by the freezing-point curve of pure molybdenum.

Uses of Temperature–Concentration Phase Diagrams. Phase diagrams are of great help in understanding the production and behavior of alloys, ceramics, and complex mixtures of organic and inorganic compounds. The presence of a maximum in the curve shows that a chemical compound is produced by the combination of two substances and gives the information regarding temperature and concentrations which is necessary to produce this compound. If there is a single eutectic point without maxima, each of the two components separates from the liquid mixture in the pure state. The presence of solid solutions is indicated when there are two curves, one for melting, one for crystallization. Many desirable properties of alloys, ceramics, and structural materials depend on the components being in the form of solid solutions. The hardening and tempering of steel involve the existence of solid solutions of carbon in different iron–carbon compounds. The solid solution stable at the high temperatures is hard, and, in order to retain this hardness, the proper compositions and temperatures are obtained, as indicated by the phase diagrams, and then the steel is quenched quickly in oil or water, so that it does not have time to form the solid solution which is stable at lower temperatures. By heating up again to a somewhat lower temperature, opportunity is given for partial conversion to the softer solid solution which is stable at the lower temperature. In this way the steel may be given different degrees of hardening.

In order to summarize several of the features of phase diagrams, the temperature–composition diagram for mixtures of gold and aluminum

is shown in **Fig. 84.*** It illustrates a more complicated alloy in which several definite chemical compounds are formed. The different compounds are indicated on the diagram, and it is evident that some of the maxima are obscured by overlapping curves. The pure compounds which correspond to the extrapolated maxima must exist only in a metastable state. There are also solid solutions of limited solubility.

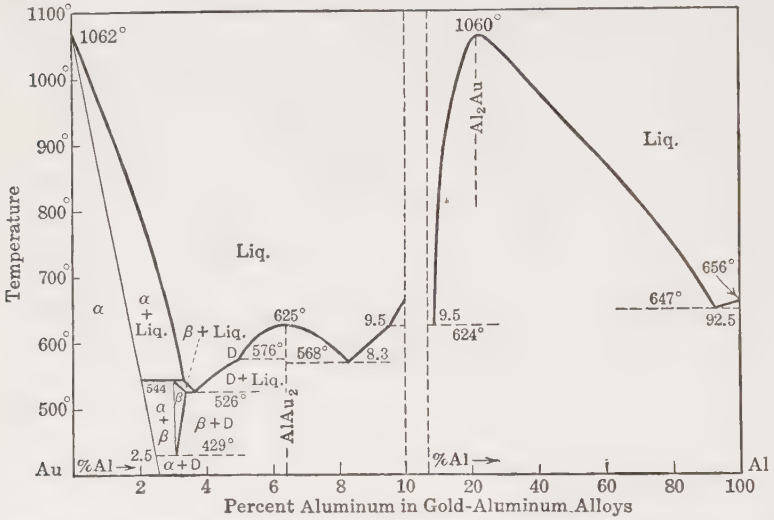


FIG. 84. Temperature–composition phase diagram for the system gold–aluminum.

Three-Component Systems. Triangular coordinates are convenient for representing the composition of a system of three components where all three must add up to 100 per cent, because, within an equilateral triangle, the sum of the distances, drawn from a point perpendicular to the three sides, is equal to the height of the triangle. In **Fig. 85** this type of diagram is used for the condensed system water, acetic acid, and vinyl acetate at 28° and constant pressure.† The point *O*, for example, represents the composition 20 per cent water, 50 per cent acetic acid, and 30 per cent vinyl acetate.

When vinyl acetate is added to water, a homogeneous solution is formed, provided that the amount of vinyl acetate does not exceed that corresponding to complete saturation, represented by the point *z*. If further amounts of vinyl acetate are added, the mixture will separate into two layers, one of which consists of a saturated solution of water

* This figure is taken from International Critical Tables, Vol. II, p. 402 (1927) with permission of the publishers, McGraw-Hill Book Co.

† Smith, *J. Phys. Chem.*, **45**, 1301 (1941).

in vinyl acetate, and the other a saturated solution of vinyl acetate in water. The composition of these two immiscible solutions is represented by the points x and z.

If acetic acid, which dissolves completely in both liquids is added, it renders the water more soluble in the vinyl acetate and the vinyl acetate more soluble in the water. It distributes itself between the two layers, forming two immiscible ternary solutions of vinyl acetate, water, and acetic acid which are in equilibrium with each other. These solutions

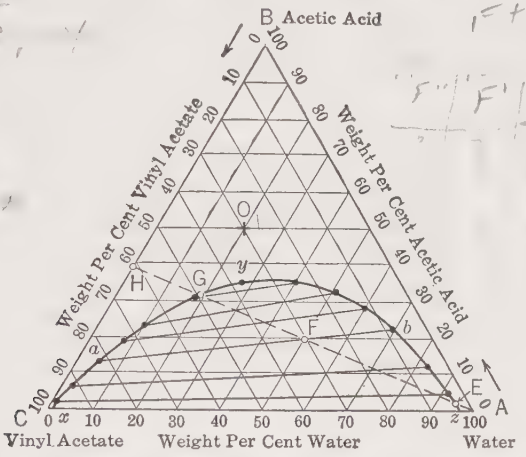


FIG. 85. Three-component phase diagram showing regions of miscibility and non miscibility plotted at 25° on triangular coordinates.

are represented by two points such as a and b within the triangular diagram. The line joining a and b is known as a *tie line*. Other tie lines are shown for other compositions; usually they are not parallel to the base AC of the triangle. The compositions of the two phases corresponding to the intersection of the tie lines with the curves xy and zy have to be determined experimentally. As more and more acid is added, the tie lines become shorter and shorter, and, ultimately, when the compositions of the two solutions become identical, they shrink to the single point y. The point y is a *critical point*, since further addition of acetic acid will result in the formation of a single homogeneous phase. Any point under the curve represents a ternary mixture which will separate into two liquid phases; any point above the curve represents a single homogeneous liquid phase.

A ternary mixture whose over-all composition is represented by the point F will separate into two conjugate ternary solutions having the compositions a and b. Significant information can be obtained by draw-

ing a line from A representing pure water, through the specified point F, and extending to cut the curve at G, and the line BC at H. Starting now with a mixture of vinyl acetate and acetic acid at H and adding water, the over-all composition of the system is given by points in succession passing from H to A. Along the line HG, the addition of water gives a single homogeneous liquid phase, in which the ratio of vinyl acetate to acetic acid is always equal to HB/HC. The percentage of vinyl acetate and acetic acid decrease as water is added, but the ratio of their percentages remains constant at 60/40. When point G is reached, the addition of more water produces two liquid phases, and these two conjugate phases persist as more water is added along the line GE. From E to A the addition of more water produces a single homogeneous phase, the water being in such large excess that the vinyl acetate and acetic acid can both dissolve in it. Between G and E the quantity of the phase which is richer in water increases relative to the quantity of the phase which has the smaller percentage of water. Not only do the relative amounts of the two different liquid phases change, but also the compositions of each phase changes as indicated by the intersections of the tie lines with the curve xyz. The over-all ratio of vinyl acetate to acetic acid in the two solutions, added together, is still, however, equal to HB/HC.

Vinyl acetate and water become more soluble at higher temperatures, and the region where there are two immiscible phases would be smaller. The line xyz would fall below its present position at higher temperatures.

In applying the phase rule to these triangular diagrams, it must be remembered that the pressure and the temperature are fixed, and in most diagrams the vapor is condensed. Then $F = C - P + O = 3 - P$.

The percentage compositions X of two of the components provide the only variables, but these may apply to several different liquid phases. When there is but one liquid phase, as in Fig. 85 above xyz, there are two degrees of freedom, namely, X_A and X_B (or X_B and X_C, or X_A and X_C), where A, B, and C are the components. When there are two liquid phases, there are four possible variables: the percentage composition of two components in the water phase and the percentage composition of two components in the vinyl acetate phase. However, according to the phase rule, only one of these variables is independent when there are two phases, since $F = 3 - 2 = 1$. With reference to the line xyz on the triangular diagram, as soon as the percentage of water in one phase is specified, the system is completely described. For example, if on the line xyz the water is specified as 5 per cent giving the point a, the composition of vinyl acetate and acetic acid in this vinyl acetate layer is

easily obtained from the triangle. Moreover, the percentage of each of the three components in the second liquid phase, the water phase, is determined by point *b* which lies at the other end of the tie line.

A common type of phase diagram is shown in **Fig. 86.** Here two different salts and water are given at the three apices of the equilateral triangle. The area at the left of the curves represents unsaturated solution. The solubility of pure $(NH_4)_2SO_4$ in per cent at 30° is given by *L*; and the solubility of pure $Li_2SO_4 \cdot H_2O$ is given by *O*. The line *LM* shows how the solubility of $(NH_4)_2SO_4$ is decreased by the addition of Li_2SO_4, and the line *ON* shows how the solubility of $Li_2SO_4 \cdot H_2O$ is changed by the addition of $(NH_4)_2SO_4$. Along the line *MN*, a double salt $Li_2SO_4 \cdot (NH_4)_2SO_4$ precipitates out. The tie lines give the composition of the solution which is in equilibrium with the salt for any total composition specified within these areas.

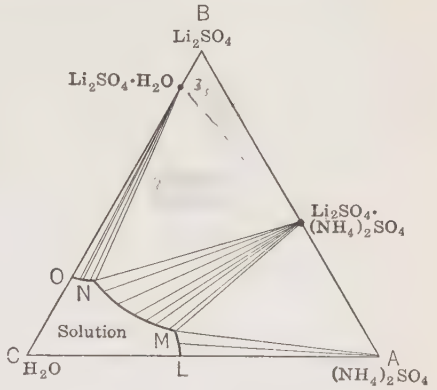


FIG. 86. Triangular diagram showing regions of solubility and double salt formation for two salts in water.

It is possible to represent temperature as a variable in a three-component system using a triangular prism in which the temperature is plotted at right angles to the base of the prism. Such prisms are useful in determining the composition of a three-metal alloy which will give the lowest possible melting point. Low-melting alloys are used, for example, in automatic water sprinklers for fire protection.

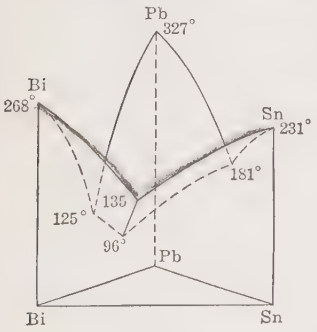


FIG. 87. Triangular prism showing solid and liquid phases for a three-component system at different temperatures.

In **Fig. 87** the temperature is plotted vertically. The front plane gives the freezing-point curves of bismuth and tin with a eutectic at 135°; the plane at the left of the back gives the freezing-point curves for bismuth and lead with a eutectic at 125°; and the remaining plane for lead and tin gives a eutectic at 181°. These curves are connected by three surfaces which meet in a point giving a eutectic at 96°, where all three metals freeze out together. This is the lowest possible melting temperature

that can be obtained from any mixture of these three metals, and the exact composition of this ternary alloy is found by projecting a vertical line down from this point until it hits the triangular base.

Some three-component systems may be represented with rectangular coordinates at various temperatures by space models of the type shown in **Fig. 88*a***. The per cent by weight of ammonium sulfate in aqueous solution is plotted along the X axis, the percentage of sodium sulfate is plotted along the Z axis, and temperature is plotted along the Y axis at right angles to the two concentration axes. The meaning of this space model is made apparent by the three graphs which accompany the model. The left side of the model is shown at *c*, where the concentration of ammonium sulfate is zero. The figure gives simply the concentration–temperature graph for sodium sulfate in water. It shows the solubility curve of Na_2SO_4 and of $Na_2SO_4 \cdot 10H_2O$ and the freezing-point curve along which ice separates. The bottom of the model shown at *d* gives the concentration–temperature graph for ammonium sulfate, and the solubility curve and the freezing point are shown intersecting at the eutectic point. In Fig. 88*b* three isothermal planes are shown intersecting the space model at 15°, 35°, and 60°. The model is constructed by placing Figs. 88*c* and 88*d* at right angles and spacing the isothermal concentration curves shown at *b* for the two salts at the proper intervals along the temperature axis. If desired, plaster of paris or other plastic material could be used to construct a space model along the curves given in these three dimensions.

The isothermal section at 15° is labeled *LMNO* in Figs. 88*a* and *b*. The solubility of $Na_2SO_4 \cdot 10H_2O$ in pure water at 15° is 11 per cent by weight. As $(NH_4)_2SO_4$ is added to the solution, the solubility of $Na_2SO_4 \cdot 10H_2O$ increases along the line *LM*. When the solution contains 21 per cent $(NH_4)_2SO_4$, the solubility of $Na_2SO_4 \cdot 10H_2O$ is 16.5 per cent (expressed as per cent of Na_2SO_4). When more ammonium sulfate is added, a double salt makes its appearance along *MN*, and, the more ammonium sulfate is added, the lower is the solubility of this double salt. The line *NO* represents the decrease in solubility of $(NH_4)_2SO_4$ at 15° caused by the addition of Na_2SO_4 to the solution. Similar curves are shown for 35° and 60°. In the space model shown in Fig. 88*a* the pressure is fixed, and the vapor is considered to be condensed. All the volume inside the space model refers to unsaturated salt solution. It is the only phase present, and there are three degrees of freedom. Percentages of two components in the solution and temperature must be specified in order to define the system completely. ($F = 3 - 1 + 1 = 3$.) The various solid phases touching the model are specified on the model. For example, on top of the model there is

Na_2SO_4, at the right there is $(NH_4)_2SO_4$, over the curved face is the double salt $Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$, and in front of the model is ice. At these surfaces there are two phases (solution and a solid phase).

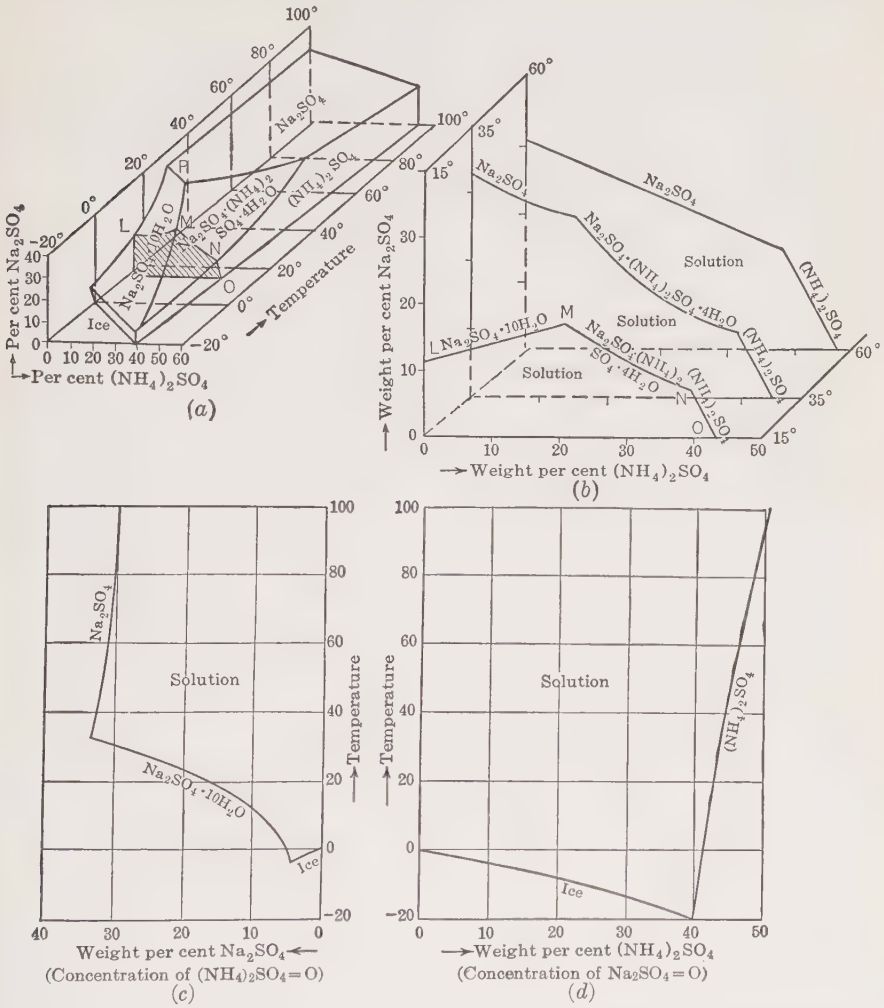


FIG. 88. Space model for two salts and water showing phases present at different concentrations of salts and at different temperatures.

Along the lines there are three phases, and at the points of intersection there are four phases. The degrees of freedom are, respectively, 2, 1, and 0. For example, at the point P there are Na_2SO_4, $Na_2SO_4 \cdot 10H_2O$, $Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$ and solution; then $F = 3 - 4 + 1 = 0$.

It is possible to represent on two-dimensional coordinate paper the proportions of many components using a method proposed by Lodochnikov and modified by Reimers.* A single axis or composition line is used for the total composition, and segments are plotted for various proportions of constituents, making use of special symbols.

REFERENCES

Bowden, "The Phase Rule and Phase Reactions," Macmillan Co., New York, 1938.

Deming, An Introduction to the Phase Rule, *J. Chem. Educ.*, **16**, 215, 260 (1939).

Findlay and Campbell, "The Phase Rule and Its Applications," Longmans, Green & Co., New York, 1938; Dover Publications, New York.

Hill (in Taylor's) "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931, Chapter IX.

Blasdale, "Equilibria in Saturated Salt Solutions," Chemical Catalog Co., New York, 1927.

Purdon and Slater, "Aqueous Solutions and Phase Diagrams," Edward Arnold & Co., London, 1946.

Briggs, "Phase Diagrams and the Mass Law," *J. Chem. Educat.*, **20**, 484 (1943).

PROBLEMS

1. Construct and interpret the phase diagram based on the following data where N_{PbI_2} is the mole fraction of lead iodide and t is the freezing point of the solution in degrees centigrade for the system KI − PbI_2:

N_{PbI_2}	1.00	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10	0.0
$t°$	412	395	367	324	337	349	422	504	585	641	686

Assume that all compositions below 0.5 N_{PbI_2} give a final solidification temperature of 346°.

Ans. Compound KI·PbI_2 melting at 349°.
Eutectics at 0.47 N_{PbI_2} and 346° and 0.69 N_{PbI_2} and 321°.

2. Interpret the diagram of the mixed phosphates shown in Fig. 89, and state the number of degrees of freedom at a typical line, point, and area. State what will happen on cooling a typical concentration of the fused phosphate mixture.

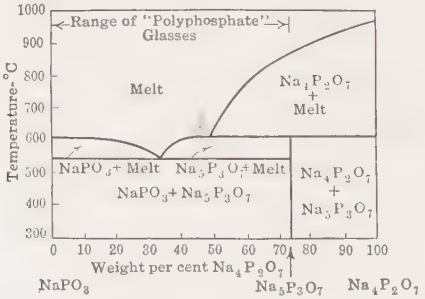


Fig. 89. Temperature–concentration phase diagram for phosphate glasses.

* Reimers, "A System of Graphics for Chemical Compositions," Dow Chemical Co., Midland, Mich., 1946.

3. The following cooling curves have been found for the system antimony–cadmium.

Per cent cadmium by weight	0	20	37.5	47.5	50	58	70	93	100
First break in curve, °C	...	550	461	....	419	...	400	...	...
Continuing constant temp, °C	630	410	410	410	410	439	295	295	321

Construct a phase diagram assuming that no other breaks than these actually occur in any cooling curve. Label the diagram completely and give the formula of any compound formed. *Ans.* Cd_3Sb_2 melting at 439°.

4. The following are the data for the system methylcyclohexane–aniline–*n*-heptane at 1 atm and 25°. Draw a triangular diagram for the system, including tie lines, and compute the exact composition of the first drop of the second liquid phase which would separate if pure aniline is added to a 40 per cent solution of methylcyclohexane in *n*-heptane until separation into two phases occurs.

Hydrocarbon Layer		*Aniline Layer*	
Wt. % Methylcyclohexane	Wt. % *n*-Heptane	Wt. % Methylcyclohexane	Wt. % *n*-Heptane
0.0	92.0	0.0	6.2
9.2	83.0	0.8	6.0
18.6	73.4	2.7	5.3
33.8	57.6	4.6	4.5
46.0	45.0	7.4	3.6
59.7	30.7	9.2	2.8
73.6	16.0	13.1	1.4
83.3	5.4	15.6	0.6
88.1	0.0	16.9	0.0

Ans. 36.7 per cent methylcyclohexane, 55.2 per cent *n*-heptane, 8.5 per cent aniline.

5. The vapor pressure of a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 8H_2O$ as a function of the temperature is given below. (*a*) Find graphically the heat of transition between these hydrated salts at 25°.

Temp.	34	30	25	20	15	10°
p	7.54	5.95	4.15	2.92	2.00	1.36 mm

(*b*) What is the free-energy change at 25° in the reaction,

$$Zn(NO_3)_2 \cdot 8H_2O\ (s) = Zn(NO_3)_2 \cdot 6H_2O\ (s) + 2H_2O\ (l)$$

(*c*) What is the entropy change in the reaction at 25°?

Ans. (*a*) ΔH = 25,000 cal.
(*b*) ΔF = 2,030 cal.
(*c*) ΔS = 7.3 e u.

---

6. (*a*) Referring to Fig. 79 choose two areas, two lines, and two points, and state what components and what phases are present. (*b*) State how many degrees of freedom there are at each of these areas, lines, and points. (*c*) Name the solid and liquid phases which appear in succession as water vapor is pumped away from a dilute solution of sulfuric acid which is maintained at −30° C.

7. Sketch a phase-rule diagram for thallium and mercury with freezing points plotted against per cent by weight. Use the following facts: Mercury melts at −39°; the compound Tl_2Hg_5 melts at 15°; thallium melts at 303°; thallium lowers the freezing point of mercury down to a minimum of −60° at a composition of 8 per cent thallium; the eutectic point for Tl and Tl_2Hg_5 is 0.4° at a composition corresponding to 41 per cent thallium. Label the phases present at each area, line, and point.

8. Given the system water, KNO_3, and $NaNO_3$ at 25°. Sketch this system on a triangular diagram, labeling the areas in which you would expect to find (*a*) only solution; (*b*) a mixture of solution and solid KNO_3; (*c*) a mixture of solution and solid $NaNO_3$; (*d*) a mixture of solid KNO_3, $NaNO_3$, and solution. The solubility of KNO_3 in pure water is 46.2 per cent, the solubility of $NaNO_3$ in pure water is 52.2 per cent, and all three of these phases are in equilibrium when the composition is as follows: water 31.3 per cent, KNO_3 28.9 per cent, and $NaNO_3$ 39.8 per cent. No crystalline hydrates nor double salts are formed.

9. The following data are available for the system $NiSO_4$—H_2SO_4—H_2O at 25°. Sketch the phase diagram on triangular coördinate paper, and draw appropriate tie lines.

Liquid Phase		*Composition of Solid Phase*
Wt. % $NiSO_4$	Wt. % H_2SO_4	
28.13	0	$NiSO_4 \cdot 7H_2O$
27.34	1.79	"
27.16	3.86	"
26.15	4.92	$NiSO_4 \cdot 6H_2O$
22.26	7.93	"
15.64	19.34	"
10.56	44.68	"
9.65	48.46	$NiSO_4 \cdot H_2O$
2.67	63.73	"
0.23	72.38	"
0.12	91.38	"
0.11	93.74	$NiSO_4$
0.08	96.80	"

10. The following data are available for the system Na_2SO_4 — $Al_2(SO_4)_3$ — H_2O at 42°. Draw the phase diagram on triangular coordinate paper, and draw in some appropriate tie lines.

Liquid Phase		*Composition of Solid Phase*
Wt. % Na_2SO_4	Wt. % $Al_2(SO_4)_3$	
33.20	0	Na_2SO_4
32.00	1.52	Na_2SO_4
31.79	1.87	Na_2SO_4
28.75	1.71	$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 14H_2O$
24.47	2.84	$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 14H_2O$
16.81	5.63	$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 14H_2O$
10.93	10.49	$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 14H_2O$
4.72	17.11	$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 14H_2O$
1.75	18.59	$Al_2(SO_4)_3$
0	16.45	$Al_2(SO_4)_3$

11. The vapor pressure of a mixture of $Zn(NO_3)_2 \cdot 4H_2O$ and $Zn(NO_3)_2 \cdot 2H_2O$ is given as a function of temperature below. Find ΔH^0, ΔF^0, and ΔS^0 at 25°.

Temp., °C	39	38	37	35	30	25	20
p, mm	2.42	2.25	1.80	1.25	0.65	0.27	0.08

12. Calculate the solubility of monoclinic sulfur in CCl_4 at 25°. That of rhombic sulfur is 0.84 g per 100 g of CCl_4. Sulfur exists in both solutions as S_8. The free energy of formation of monoclinic sulfur is 23 cal per mole greater than that of rhombic sulfur at 25°.

13. Interpret the phase diagrams for the polyiodides of cesium published by Briggs and Hubbard, *J. Phys. Chem.*, **45,** 821 (1941).

14. Interpret the phase diagram for the iron–carbon system given on page 609 of Vol. II of International Critical Tables.*

15. Interpret the three-dimensional model representing the system aniline–sulfur dioxide, as worked out by Hill and shown in **Fig. 90.** (*J. Am. Chem. Soc.*, **53,** 2598 [1931].)

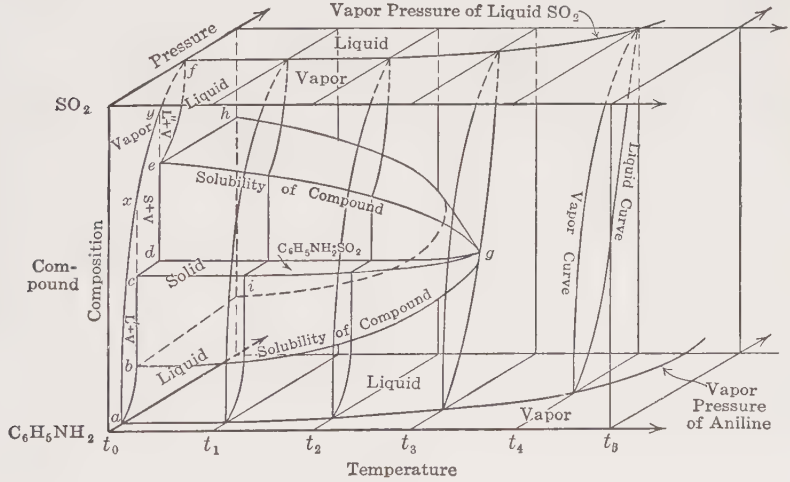


Fig. 90. Concentration–temperature–pressure phase diagram.

* McGraw-Hill Book Co., New York, 1927.

CHAPTER XIV

CHEMICAL KINETICS

The aim of chemical kinetics is to predict the rates of chemical reactions and to describe the course of the reactions. It is a more difficult field than thermodynamics and the prediction of chemical equilibria, because the latter are concerned only with the initial and final states and not with time nor with mechanisms, nor with intermediate states. Science has not progressed very far in chemical kinetics, but the mere fact that the study of kinetics is a pioneer field adds interest to the subject. Many processes involve two or more reactions which are going on simultaneously in a very complicated manner. Impurities and traces of catalysts are likely to change the velocities, so that it is often difficult to obtain reproducible results.

Most ionic reactions of inorganic chemistry take place so fast that their rates cannot be measured, but in many of the reactions of organic chemistry the study of chemical kinetics is particularly important. Most reactions of organic chemistry are slow, and the relative rates of competing reactions are often more important considerations than is the extent to which the reactions are completed at equilibrium. If two organic substances are mixed together, there may be many different products which are all possible according to thermodynamics. By altering the concentrations and the temperature and by using specific catalysts, it is possible to bring about a desired reaction. If the specified reaction cannot be made much faster than all the other competing reactions, the yield will be low.

Experimental Measurements of Reaction Rates. The rate of a chemical reaction may be followed in many different ways. Samples may be removed at intervals, chilled rapidly, and analyzed by titration or other analytical methods. Again, several bulbs of reacting material may be started out together, and each may be chilled quickly at different time intervals and analyzed. The chilling must be so rapid that the concentration does not change appreciably during the sampling operation.

Physical means of analysis which do not disturb the system are convenient. If one of the reactants or products rotates the plane of polarized light, its concentration may be determined during the course of

the reaction with the help of a polarimeter. Again, the concentration of one of the materials may be followed by measuring the absorption of light at a given wave length and applying Beer's law. Frequently, this method is not practical, because more than one colored material is present. The use of ultraviolet and infrared light makes possible wider applications of this method.

An increase in volume of a solution measured during the course of the reaction may be followed in a large thermometer bulb or a dilatometer. Again, the volume of gas evolved by certain reactions in a liquid solution may be taken as a measure of the extent of the reaction. The volume V_0 is measured at the beginning and the volume V_∞ when the reaction has been completed. Measurements of volume V_t are taken at various times t during the reaction. Then $V_\infty - V_0$ is a measure of the total amount of material which can react, and $V_\infty - V_t$ is the measure of the amount of material which still remains unreacted at time t. Then, the fraction of the material remaining unreacted at time t is given by the expression $(V_\infty - V_t)/(V_\infty - V_0)$.

Example 1. When nitrogen pentoxide decomposes in carbon tetrachloride solution, oxygen gas is evolved. In one experiment 23.95 ml of gas was evolved during 1 hour's time and, after standing till no more gas was given off, the total volume of the gas was 34.75 ml. What fraction of nitrogen pentoxide remained undecomposed after 1 hour?

$$\text{Fraction undecomposed} = \frac{34.75 - 23.95}{34.75} = 0.311$$

Electrical conductivity of a solution and total pressure of a gas are other physical properties which may be used in a similar manner to follow the rate of a chemical reaction. In complicated reactions, however, it is unwise to use total pressure as a measure of the extent of decomposition, unless the measurements are accompanied by chemical or physical analyses which are specific for one or more of the reacting materials.

Example 2. In the gaseous reaction $C_2H_5Br \rightarrow C_2H_4 + HBr$, the pressure increased from 200 mm at the beginning to 390 mm at the end. After 500 seconds the pressure was 300 mm. What fraction remained undecomposed? If it is assumed that the pressure should double to 400 mm at the end, as indicated by the equation, half of the material would be left, that is, $(400 - 300)/200 = 0.50$. However, the fact that the final pressure was 10 mm less than 400 mm indicates that there is some complication involved, and the calculation is not entirely safe. Obviously, some other reaction in addition to the one written on paper is involved.

The rate of a reaction may be determined by measuring either the rate of decrease of the reactants or the rate of increase of the products.

The rate of increase of concentration is represented by dc/dt, and the rate of decrease in concentration is represented by $-dc/dt$. In gas reactions a stream of reacting materials is sometimes passed through a reaction vessel in a steady flow. The volume of the vessel divided by the volume of the gases passing through the vessel in 1 second gives a measure of the time in seconds during which the gases are in the vessel. The vessel may be heated to a higher temperature, or it may be filled with a catalyst. The gases entering the vessel and issuing from it are analyzed. It is difficult to get exact kinetic data by the flow method, but it makes possible the use of large quantities of material, and it is a common industrial operation.

Example 3. A volume of 1200 ml of gas is passed through a 100-ml heated tube in 300 seconds. The volume is the calculated volume of the gas at the temperature of the furnace. Approximately how long is each molecule exposed to this higher temperature?

The flow of gas is $\frac{1200}{300}$ or 4 ml per second. The time t of residence of the gas in the tube is given by the calculation:

$$t = \frac{100 \text{ ml}}{4 \text{ ml sec}^{-1}} = 25 \text{ sec}$$

Reaction Mechanisms. In a *unimolecular reaction* only one molecule is involved in the chemical reaction. It may break up into smaller parts as in the dissociation of bromine at high temperatures,

$$Br_2 \rightarrow 2Br$$

or it may merely undergo a rearrangement as when maleic acid is converted into fumaric by heating,

$$\begin{array}{l} H{-}C{-}COOH \\ \quad\quad\| \\ H{-}C{-}COOH \end{array} \rightarrow \begin{array}{l} \quad HCCOOH \\ \quad\quad\| \\ HOOCCH \end{array}$$

In a *bimolecular* reaction two molecules must come together before reaction can take place. They may be different kinds as in the formation of hydriodic acid,

$$H_2 + I_2 \rightarrow 2HI$$

or the same kind as in the dissociation of hydriodic acid which occurs at a higher temperature,

$$HI + HI \rightarrow H_2 + I_2$$

In the example just given one could write the reaction as a unimolecular reaction,

$$HI \rightarrow H + I$$

but the energy required to produce the free atoms of hydrogen and iodine is so great that the reaction does not ordinarily go by this mechanism.

In a termolecular reaction three molecules combine as, for example, in the reaction,

$$A + B + C \rightarrow ABC$$

or in the oxidation of nitric oxide,

$$2NO + O_2 \rightarrow 2NO_2$$

Termolecular reactions are rare, and reactions involving the simultaneous collision of more than three reactants are never found.

Most reactions are quite complex and really involve a series of steps, some fast and some slow, but each of these steps is usually itself a unimolecular or bimolecular reaction. For example, the thermal decomposition of ethyl bromide may be written simply as the unimolecular reaction:

$$C_2H_5Br \rightarrow C_2H_4 + HBr$$

The stoichiometrical quantities are given correctly by the equation, but the reaction may involve a series of steps with atoms and fragments such as the following:

$$C_2H_5Br \rightarrow C_2H_5 + Br$$

$$Br + C_2H_5Br \rightarrow HBr + C_2H_4Br$$

$$C_2H_4Br \rightarrow C_2H_4 + Br$$

The over-all reaction as written on paper usually has little significance in chemical kinetics. It is more important to learn by experiment how the rate of the reaction is influenced by the concentration of the reacting materials and, thus, to establish the *order* of the reaction as described in the following sections.

First-Order Reactions. A *first-order reaction* is one in which the rate of reaction is found by experiment to be directly proportional to the concentration of the reacting substance. Obviously the amount of material which reacts depends on the amount that is present, and, if the volume is kept constant, the situation is described mathematically as follows:

$$-\frac{dc_A}{dt} = kc_A \tag{1}$$

where c is the concentration of reacting material A, k is a proportionality factor, t is the time, and $-dc/dt$ is the rate at which the concentration decreases.

Integrating this simple differential equation, we have

$$-\ln c_A = kt + \text{constant}$$

$$-\log c_A = \left(\frac{k}{2.303}\right) t + \text{constant} \tag{2}$$

It is evident from this equation that in a first-order reaction a straight line is produced when the logarithm of the concentration is plotted against time. The velocity constant k can be evaluated by multiplying the slope of the line by 2.303.

Integrating equation 1 between the limits, concentration c_1 at time t_1, and c_2 at a later time t_2, we have

$$-\int_{c_1}^{c_2} \frac{dc}{c} = k\int_{t_1}^{t_2} dt$$

$$-\ln c_2 - (-\ln c_1) = k(t_2 - t_1)$$

$$k = \frac{2.303}{t_2 - t_1} \log \frac{c_1}{c_2} \tag{3}$$

This equation may be modified to give the following equation:

$$k = \frac{2.303}{t} \log \frac{c_0}{c} \tag{4}$$

where c_0 is the concentration at the beginning of the reaction when the time is zero and c is the concentration after time t has elapsed.

This equation is often written in the exponential form:

$$c = c_0 e^{-kt} \tag{5}$$

Still another modification is used, in which a is the initial quantity of reacting material A in a given volume, x is the amount reacting in time t, and $a - x$ is the amount remaining after time t. Then,

$$\frac{dx}{dt} = k(a - x) \tag{6}$$

and

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \tag{7}$$

The constant k is called the *specific reaction-rate constant* or the *velocity constant*. For a first-order reaction it is a number per unit of time and may be expressed in reciprocal seconds (or in other units of time).

When, for example, k has a value of 0.001 sec^{-1} the material is decomposing at the rate of 0.1 per cent per second.

Reaction rates may be described by giving the numerical value of k, or sometimes by giving the *period of half-life*, $t_{½}$, that is, the time necessary for half a given quantity of material to decompose. It is meaningless to speak of the time necessary for all the material to decompose, because, theoretically, an infinite time is required. For a first-order reaction,

$$k = \frac{2.303}{t_{½}} \log \frac{1}{\frac{1}{2}} = \frac{0.693}{t_{½}}$$

The period of half-life in a first-order equation then is

$$t_{½} = \frac{0.693}{k} \qquad (8)$$

The determination of the specific rate constant makes possible a calculation of the amount of material which will react in a given time, or the time required for any specified portion of the material to react.

The calculation of first-order reaction rates may be illustrated with the decomposition of nitrogen pentoxide.* Nitrogen pentoxide is a crystalline solid which gives a gaseous pressure of 1 atm at about 30°. It decomposes completely in the gas phase, or when dissolved in inert solvents, at a rate which is conveniently measured at room temperature. It is strictly first order, and its rate of decomposition has been checked in many different laboratories. The end products are oxygen and a mixture of N_2O_4 and NO_2. The following equation represents the over-all reaction, although the intermediate steps are probably quite complicated (as they are in most reactions which have been thoroughly studied):

$$\begin{array}{c} N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2 \\ \downarrow\uparrow \\ 2NO_2 \end{array}$$

For every molecule of oxygen produced, two molecules of nitrogen pentoxide have decomposed.

When a solution of nitrogen pentoxide in carbon tetrachloride decomposes, the N_2O_4 and NO_2 remain in solution while the oxygen escapes and is measured in a gas buret. The reaction vessel is carefully thermostated, and it is agitated to prevent supersaturation.

* Daniels and Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921); Eyring and Daniels, *ibid.*, **52**, 1472 (1930).

Experimental data for the decomposition of nitrogen pentoxide dissolved in carbon tetrachloride at 45° were calculated as illustrated in example 1. They are given in Table I and plotted in the accompanying figures.

TABLE I

DECOMPOSITION OF N_2O_5 IN CCl_4 SOLUTION AT 45°

t (seconds)	c (moles/liter)	log c	$-\frac{\Delta c}{\Delta t}$	Average c	k equation 4 $\times 10^4$
0	2.33	0.367	.....	....	....
184	2.08	0.318	0.00136	2.20	6.32
319	1.91	0.281	0.00126	2.00	6.23
526	1.67	0.223	0.00116	1.79	6.22
867	1.36	0.133	0.00090	1.51	6.23
1198	1.11	0.045	0.00075	1.23	6.03
1877	0.72	$\bar{1}$.857	0.00057	0.92	6.27
2315	0.55	$\bar{1}$.740	0.00039	0.64	6.42
3144	0.34	$\bar{1}$.531	0.00028	0.44	5.88

In **Fig. 91*a*** the concentration is plotted against time where it is seen that the concentration decreases with time, rapidly at first, then more slowly, and finally approaches zero.

In **Fig. 91*b*** the straight line produced by plotting the logarithm of the concentration against time shows that the reaction is first-order and follows strictly the relation given by equation 2.

In **Fig. 91*c*** the values of $-\Delta c/\Delta t$ obtained by taking increments of concentration and time between successive observations are plotted against the average concentration. The increments are sufficiently small so that the graph constitutes a confirmation of equation 1 and gives a straight line which runs into the origin. It shows that the rate of decrease in concentration with time is proportional to the concentration.

The value of the specific reaction rate, as given in the last column of Table I, ranges around 0.00062. The best value is 0.000622 as obtained by multiplying the slope of the line in Fig. 91*b* by 2.303, in agreement with equation 2. The slope of the straight line in Fig. 91*c*, which is k in agreement with equation 1, has a value of 0.00062.

Sometimes it is inconvenient and unnecessary to determine so many points on the curve. If the reaction is first order, it will take twice as

long for three fourths of the material to decompose as it takes for half of it to decompose. This single criterion is sometimes useful.

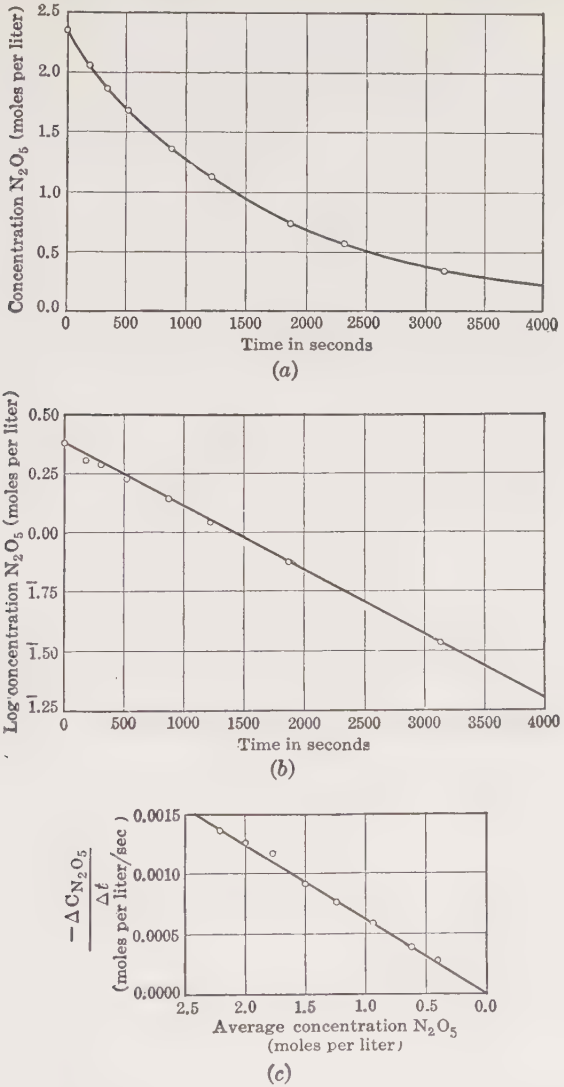


FIG. 91. Three different ways of showing the decrease in concentration of material with time in a first-order reaction.

After proving that the reaction is strictly first order, the best value of the constant k can be determined from the slope of the straight line as in Fig. 91*b* or by substituting two widely separated readings into for-

mula 3. The best results are obtained when the first reading is chosen near the beginning of the experiment, as soon as the reaction vessel has reached the temperature of the thermostat, and the second one when the reaction is about two thirds completed. In this way the errors of experimental measurement are reduced to a minimum. Two other independent readings over about the same range may be used as a check. It is not satisfactory to average all the constants obtained in successive time intervals using formula 3, for such a procedure may cancel out all the intermediate readings and give a constant based only on the first and last readings. These readings are often the least accurate.*

Second-Order Reactions. When the rate of a reaction as determined in the laboratory is proportional to the concentration of two reacting substances, the reaction is of the second order. Thus, in the reaction $A + B \rightarrow AB$, if

$$-\frac{dc_A}{dt} = -\frac{dc_B}{dt} = kc_Ac_B \tag{9}$$

the reaction is said to be of the second order. It will be shown on page 362 that if

$$\frac{-dc_A}{dt} = kc^2{}_Ac^\circ{}_B$$

the reaction would be classed also as second order.

If a and b represent the initial molar concentrations of the two reacting substances, and if x denotes the number of moles of A or B in each liter reacting in the interval of time t, then the velocity of the reaction is expressed by the equation:

$$\frac{dx}{dt} = k(a - x)(b - x) \tag{10}$$

In the simplest case the two substances (A and B) are present in equal concentrations, and $a = b$. Under these conditions, the rate equation becomes

$$\frac{dx}{dt} = k(a - x)^2 \tag{11}$$

Integrating equation 11 yields

$$\frac{1}{a - x} = kt + C \tag{12}$$

* Mathematical methods for calculating rate constants are discussed critically by Roseveare, *J. Am. Chem. Soc.*, **53**, 1651 (1931); and by Reed and Theriault, *J. Phys. Chem.*, **35**, 673 (1931).

Evaluating the integration constant C by setting $x = 0$ when $t = 0$, we have

$$k = \frac{1}{t} \cdot \frac{x}{a(a - x)} \tag{13}$$

If the reacting substances are not present in equivalent amounts, then equation 10 must be employed. On integrating * and evaluating the integration constant, this becomes

$$kt = \frac{1}{a - b} \ln \frac{b(a - x)}{a(b - x)}$$

or

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)} \tag{14}$$

The graphical method for obtaining the best value of k is convenient and satisfactory unless the data are so accurate that the errors of graphing are greater than the experimental error. Usually the experimental errors are greater. When $\log [b(a - x)/a(b - x)]$ † is plotted as ordinates against t, a straight line is obtained if the reaction is second order, and k is then obtained by multiplying the slope of the line by $2.303/(a - b)$.

The value of k in a second-order reaction depends on the units in which the concentration is expressed, since the magnitude of the term $(a - b)$ depends on the units used. For the sake of uniformity it is customary to express concentrations in moles per liter. The constant k has the dimensions liters moles^{-1} sec^{-1}. In a first-order reaction the form of the equation is such that the units of concentration cancel out.

The hydrolysis of an ester by an alkali may be taken as an illustration of a second-order reaction. The reaction,

$$CH_3COOC_2H_5 + OH^- \rightleftharpoons CH_3COO^- + C_2H_5OH$$

has been studied by several investigators. Reactions of this type may be followed in a number of different ways. Solutions of ester and alkali are placed in separate flasks in a thermostat and then mixed. At frequent intervals, a portion of the reaction mixture is removed, discharged into standard acid, and back-titrated with standard alkali. A final titration after the reaction is completed is necessary to determine the initial concentrations. The reaction may be followed also by measuring the change in the electrical conductance of the system, as already

* Daniels, "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., New York, 1928, page 189.

† This may be replaced for purposes of graphing by its equivalent $\log [(a - x)/(b - x)] + \text{constant}$.

explained or by measuring the slight increase in volume of the liquid as the reaction proceeds.

Experimental data obtained by titration are recorded in the first three columns of Table II, and the specific rate constant k is given in the last column, as calculated by equation 14.

TABLE II

HYDROLYSIS OF ETHYL ACETATE AT 25°

a = concentration of NaOH = 0.00980 mole per liter
b = concentration of $CH_3COOC_2H_5$ = 0.00486 mole per liter

Time, seconds	$a - x$ (moles/liter)	$b - x$ (moles/liter)	$\log \frac{b(a-x)}{a(b-x)}$	$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$
0	0.00980	0.00486	.....	.....
178	0.00892	0.00398	0.0412	0.108
273	0.00864	0.00370	0.0640	0.109
531	0.00792	0.00297	0.1208	0.106
866	0.00724	0.00230	0.1936	0.104
1510	0.00645	0.00151	0.3266	0.101
1918	0.00603	0.00109	0.4390	0.106
2401	0.00574	0.00080	0.5518	0.107

The specific rate constant k can be determined easily and with greater accuracy by a graphical method.

Example 4. Calculate k from the data of Table II as shown in **Fig. 92.**

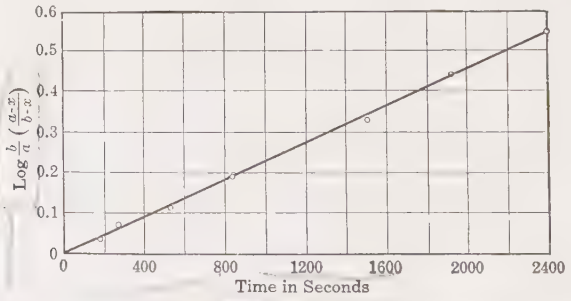


FIG. 92. Straight-line graph for a second-order reaction; the hydrolysis of ethyl acetate.

The slope of the line is 0.550/2400 = 0.000229. It is equal to $\frac{1}{t} \log \frac{b(a-x)}{a(b-x)}$. Then, since $a - b = 0.00980 - 0.00486 = 0.00494$,

$$k = \frac{2.303}{(a-b)} \frac{1}{t} \log \frac{b(a-x)}{a(b-x)} = \frac{2.303}{0.00494} \times 0.000229 = 0.107$$

Third-Order Reactions. If in a reaction involving three substances A, B, and C,

$$-\frac{dc_A}{dt} = -\frac{dc_B}{dt} = -\frac{dc_C}{dt} = kc_Ac_Bc_C \tag{15}$$

the reaction is called a third-order reaction.

It is helpful in studying reaction rates to assign symbols to the original concentrations and let x refer to the change in concentration during the reaction up to time t. In this way the absolute concentration of the reacting materials can be calculated more easily.

Then equation 15 may be written

$$\frac{dx}{dt} = k(a - x)(b - x)(c - x) \tag{16}$$

and, in the special case where $a = b = c$,

$$\frac{dx}{dt} = k(a - x)^3$$

and

$$\frac{1}{2(a - x)^2} = -kt + \text{constant} \tag{17}$$

The oxidation of nitric oxide to nitrogen dioxide

$$2NO + O_2 = 2NO_2$$

is a third-order reaction,* because the rate equation is found to be

$$\frac{dc_{NO_2}}{dt} = kc_{NO}{}^2c_{O_2}$$

Zero-Order Reactions. There are reactions also in which the rate is unaffected by the concentration, because it is determined by some other limiting factor such as the absorption of light in certain photochemical reactions or the rate of diffusion in certain surface reactions.

$$-\frac{dc_A}{dt} = k' \tag{18}$$

Again, the concentration of material may be kept constant automatically as in a saturated solution. Then, although c_A is a constant, x the amount of A reacting as defined in equation 6 is given by the expression,

$$\frac{dx}{dt} = k' \tag{19}$$

$$x = k't + \text{constant} \tag{20}$$

* Hasche and Patrick, *J. Am. Chem. Soc.*, **47**, 1207 (1925).

The constant k' calculated in this way may include arbitrary constants corresponding to the fixed intensity of absorbed light or the concentration in a saturated solution or vapor.

Example 5. At 25° the pressure p of N_2O_5 in equilibrium with crystalline N_2O_5 is 414 mm. The solid N_2O_5 does not decompose, but the gaseous N_2O_5 decomposes slowly, giving 1 molecule of oxygen for every 2 molecules of N_2O_5 decomposed. When a molecule decomposes, its place is taken by another molecule from the crystal, and, thus, the concentration of gaseous N_2O_5 is maintained constant. The pressure of oxygen increased at 25° as given by the following data. Calculate the specific decomposition rate k.

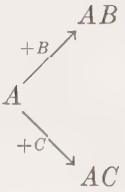
Time, seconds	0	1200	1800	2400	3000	3600
O_2 formed, mm	0	7.0	11.7	17.1	20.2	24.5
N_2O_5 decomposed, mm	0	14.0	23.5	34.3	40.4	49.0
$k' = N_2O_5$ decomposed sec^{-1} (mm $\times 10^2$)	0	1.17	1.30	1.43	1.34	1.36
k = specific decomposition rate $N_2O_5 = \frac{k'}{414}$ ($\times 10^5$)		2.8	3.1	3.4	3.2	3.3

Complex Reactions. The mathematical description of reaction rates thus far has been confined to a few standard types, but it must not be imagined that most chemical reactions are amenable to such simple mathematical treatment. In fact, there are very few chemical reactions which follow first-, second-, or third-order equations throughout the whole course of the reaction. More often there are two or more different reactions taking place at the same time so that the mathematical description of the over-all reaction is the resultant of several different rate expressions. Important among the complications are *consecutive reactions*, *reverse reactions*, and *competing reactions*, some types of which are illustrated here.

Consecutive reactions: $A \rightarrow B \rightarrow C$

Reverse reactions: $A_2 + B_2 \rightleftarrows 2AB$

Competing reactions:



These several reactions are either unimolecular or bimolecular reactions, and occasionally perhaps termolecular. It is clear that, although the individual reactions are simple unimolecular or bimolecular reactions

which follow the first- or second-order equations, the over-all reaction may be exceedingly difficult to describe mathematically because several of the consecutive, reverse, and competing reactions may be going on at the same time. Accordingly, the chemical reactions chosen for laboratory study are usually ones in which all but one of the reactions are negligible, because they are either too fast or too slow to be of significance in comparison with the one reaction. In general, the accuracy of rate measurement is not high, and it is safe to ignore those reaction steps which do not contribute more than about 1 per cent to the over-all concentration.

For example, in consecutive reactions $A \rightarrow B \rightarrow C$, if the reaction $B \rightarrow C$ is fast (perhaps 100 times as fast), in comparison with the slow reaction $A \rightarrow B$, the latter will be the determining rate.

Consecutive reactions are very common. In fact, the equations as ordinarily written give little idea of the intermediate steps, and yet one of these intermediate steps may be the slowest reaction, that is, the rate-determining reaction. Kinetic measurements offer one of the best methods for studying intermediate steps in a reaction. Simple reactions, like the oxidation of hydrocarbons to give carbon dioxide and water, really pass through a series of intermediate stages involving the production of peroxides, alcohols, ketones, and acids.

Many excellent examples of consecutive first-order reactions are found among the nuclear reactions of the radioactive elements (page 629). Because these radioactive reactions are unaffected by temperature, pressure, or catalysts, and other factors, they can be expressed with exactness by simple first-order equations.

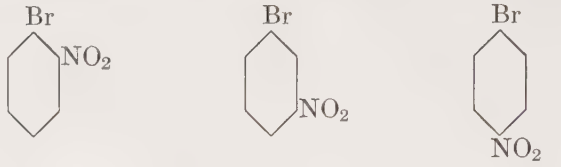
Theoretically, all reactions are reversible, but, usually, the reverse reaction can be ignored because it does not affect the final concentration appreciably. An example of a reversible reaction is

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O$$

At first, the reverse reaction can be ignored, but, after appreciable amounts of ethyl acetate and water have accumulated, both reactions must be included in the rate expression.

Competing reactions are very common, particularly in organic chemistry. When two compounds are mixed, there may be dozens of products all of which are possible according to the laws of thermodynamics. Of the several possible products that product which is formed by the fastest reaction will appropriate most of the reacting materials and be the predominating material. In studying chemical kinetics those reactions are usually chosen in which one reaction predominates and all other simultaneous or competing reactions are relatively much slower. In

synthesizing compounds the organic chemist chooses reactions in which he can suppress all the competing reactions and leave only the one reaction which gives the desired product. An example of competing reactions is the nitration of bromobenzene to give ortho, meta, and para nitrobromobenzene, which, under certain conditions, gives the yields indicated.



Ortho 13.5 per cent | Meta 0.3 per cent | Para 86.2 per cent

Obviously, a high conversion of bromobenzene to para nitrobromobenzene can be obtained only in case the production of the meta and ortho forms is small.

Again the reaction of chlorine to methane might give

$$xCl_2 + CH_4 \rightarrow \begin{cases} CH_3Cl \\ CH_2Cl_2 \\ CHCl_3 \\ CCl_4 \end{cases}$$

The study of kinetics should help to show which product will predominate and suggest means by which the conditions can be controlled to favor the production of one of these specified products at the expense of the others.

There are many cases in which the reaction mechanism is more complicated than appears from the simple rate equation. For example, the inversion of cane sugar in aqueous solution proceeds according to the following bimolecular equation when hydrogen ions are present:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

The rate of the reaction is followed by measuring the rotation of polarized light. Although water (and hydrogen ions) play an active part in this reaction, its concentration does not appear to change, because the water is present in large excess. For example, in a 0.5-molal solution there are 111 molecules of water to every molecule of sugar, and when the sugar has completely reacted, the water will have been reduced by less than 1 per cent. The second-order equation reduces to the simple first-order equation since one of the reactants is essentially constant.

The decomposition of hydrogen peroxide represents another type of

complex reaction. Hydrogen peroxide is fairly stable in the absence of catalysts, but, when it combines with a substance such as ferric chloride (probably to give ferric acid), the decomposition is rapid. Although the reaction involves two reacting substances, one of them, that is, the ferric chloride, is released unchanged after the reaction. The concentration of the ferric chloride remains constant and equation 9 reduces to equation 1 since c_B is constant.

Mathematical Analysis of Complex Reactions. The mathematical treatment of complex reactions will be illustrated with simple cases of consecutive first-order reactions which can be integrated by standard methods.

$$A \xrightarrow[k_1=0.1]{} B \xrightarrow[k_2=0.05]{} C$$

in which the specific reaction rates are 0.1 and 0.05 per hour, respectively. At the beginning of the reactions, it is imagined that there is 1 mole of A and none of B or C. After a time t, x moles of A have decomposed at the rate of 10 per cent per hour producing x moles of B and leaving $1 - x$ moles of A. But B also decomposes and does so at the rate of 5 per cent per hour. After time t, y moles of C have been produced. The amount of B is the result of a balance between formation and decomposition, and at any time t it is represented by $x - y$.

The decomposition rate of A is given by the equation:

$$\frac{-d(1-x)}{dt} = k_1(1-x) \tag{21}$$

The rate of formation of C is given by the equation:

$$\frac{dy}{dt} = k_2(x-y) \tag{22}$$

The amount of A at any time is obtained by integrating the first equation to give $(1 - x) = e^{-k_1 t} = e^{-0.1t}$, and the amount of C is obtained by substituting this value of x into equation 22 and solving the differential equation * to give $y = 2(1 - e^{-0.05t}) - (1 - e^{-0.1t})$. The amount of B at any time is merely the difference between x and y.

* $$\frac{dy}{dt} + k_2 y = k_2 x = k_2(1 - e^{-k_1 t})$$

$$y = \frac{k_2(1-e^{-k_1 t}) - k_1(1-e^{-k_2 t})}{k_2 - k_1} = \frac{0.05(1-e^{-0.1t}) - 0.1(1-e^{0.05t})}{0.05 - 0.1}$$

$$y = 2(1 - e^{-0.05t}) - (1 - e^{-0.1t})$$

The amounts of A, B, and C as calculated from these formulas are recorded at various times in Table III and **Fig. 93.**

TABLE III

CONSECUTIVE REACTIONS $A \xrightarrow[k=0.1]{} B \xrightarrow[k=0.05]{} C$

Amounts of A, B, and C at various times starting with 1 mole of A

Time, t	Quantity A, $(1-x) = e^{-0.1t}$	$e^{-0.05t}$	Quantity C, y	Quantity B, $x - y$
0	1	1	0	0
10	0.368	0.606	0.156	0.476
20	0.135	0.368	0.399	0.466
30	0.0498	0.223	0.604	0.346
40	0.0183	0.135	0.748	0.234
50	0.00674	0.0821	0.842	0.151
60	0.00248	0.0498	0.903	0.095

If the course of the reaction were followed by analyzing for A, curve A would be obtained; if it were followed by measuring the quantity of the end product C, curve C would result; and, finally, if only the intermediate product B were determined, the course of the reaction would rise to a maximum and then fall off, as shown by curve B. The broken line D gives the rate at which the decomposition product of A would be formed in case it did not undergo further decomposition. The actual rate of production of C is seen to be quite complicated, and the existence of a slow induction period or time lag at the beginning of the reaction is evident.

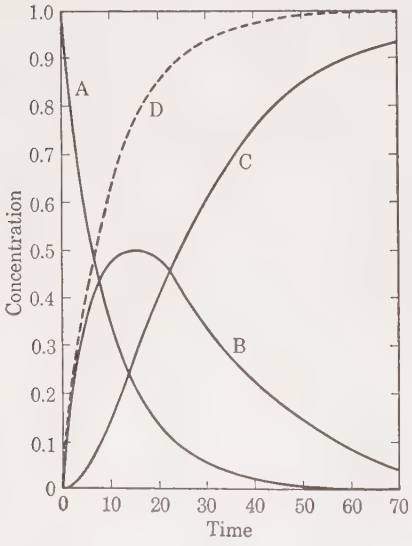


FIG. 93. Consecutive first-order reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, $k_1 = 0.1$; $k_2 = 0.05$.

This example is given in some detail because it is a comparatively simple example of a complicated reaction. When the rate of each of the steps is known, the over-all reaction rate can be built up as shown, provided it is possible or

practical to carry out the operations of integration. In laboratory practice the situation is usually much more difficult, for the over-all reaction is known, and the problem is to determine the rates of the intermediate steps. Not only is it difficult to solve the resulting differential equations, but also it is even more difficult to be sure that the set of reactions thus determined is the only set that will be in accord with the observed facts, that is, that the solution is a unique solution.

Reversible as well as consecutive reactions may be treated mathematically if the equilibrium constant is known, making allowance for the reverse reaction. Starting with a moles of acetic acid and a moles of alcohol in the reaction $CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$, the rate of the forward reaction is given by the expression,

$$\frac{dx}{dt} = k_1(a - x)^2 \tag{23}$$

where x represents the amount of acid and alcohol reacting, or the amount of ester and water formed at the time t, and k_1 is the specific reaction rate of the forward reaction.

The rate of the reverse reaction is given by the expression,

$$-\frac{dx}{dt} = k_2x^2 \tag{24}$$

where k_2 is the specific reaction rate at which the concentration of the products, ester and water, *decrease*.

The actually observed rate, including both forward and reverse reactions, is

$$\frac{dx}{dt} = k_1(a - x)^2 - k_2x^2 \tag{25}$$

But, from the definition of the equilibrium constant,

$$K = \frac{k_1}{k_2}$$

or

$$k_2 = \frac{k_1}{K} \tag{26}$$

and

$$\frac{dx}{dt} = k_1(a - x)^2 - \frac{k_1}{K}x^2 \tag{27}$$

In the reaction between acetic acid and ethyl alcohol, at room temperature, K has the value 4.0, and equation 27 may be integrated and solved for k_1.

One more example of a complex reaction is cited in **Fig. 94,** in which a first-order reaction is followed by another first-order reaction which, however, is accompanied by a reverse reaction, as follows:

$$A \xrightarrow{k_1} B \underset{k_3}{\overset{k_2}{\rightleftharpoons}} C$$

where $k_1 = 0.10$; $k_2 = 0.10$, and $k_3 = 0.05$. All the reactions are first-order reactions.

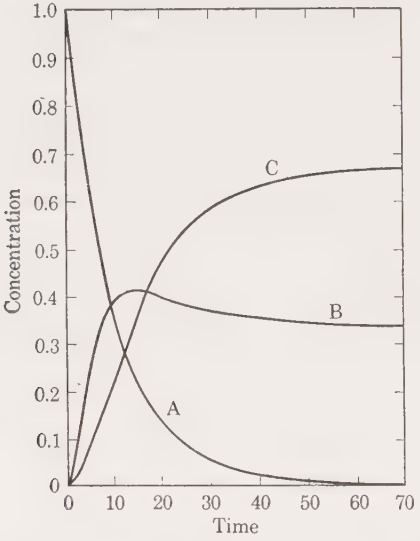


FIG. 94. Consecutive first-order reactions with reverse reaction $A \xrightarrow{k_1} B \underset{k_3}{\overset{k_2}{\rightleftharpoons}} C$, $k_1 = 0.1$; $k_2 = 0.1$; $k_3 = 0.05$.

There are many other kinetic expressions which combine competing, consecutive, or reverse reactions, each of which may involve either a first-order or a second-order equation.* Many of the more complicated ones are difficult or impossible to integrate. However, the perfection of mechanical calculators and differential analyzers and the development of elaborate calculating machines making use of multiple banks of electron tubes have made possible the solution of very complicated

* For a fuller treatment the student is referred to Moelwynn-Hughes, "Physical Chemistry," Oxford University Press, 1941, Appendix 9, and to Sherwood and Reed, "Applied Mathematics in Chemical Engineering," McGraw-Hill Book Co., New York, 1939.

kinetic equations. Often valuable information can be obtained from the rate equations without integration, and through them it is easy to understand why there are sometimes induction periods, why complex reactions may approach a first or second order or a fractional order, and why these apparent orders change during the course of the reaction.

Example 6. Set up a rate expression for the following reactions, 1 and 2, which go on simultaneously.

(1) $$A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} B + C$$

(2) $$A + B \xrightarrow{k_2} D$$

(3) $$\frac{dc_A}{dt} = -k_1 c_A + k_1' c_B c_C - k_2 c_A c_B$$

(4) $$\frac{dc_D}{dt} = k_2 c_A c_B$$

(5) $$\frac{dc_C}{dt} = k_1 c_A - k_1' c_C c_B$$

(6) $$\frac{dc_B}{dt} = k_1 c_A - k_1' c_B c_C - k_2 c_A c_B$$

It may be assumed that, after a short induction period, B is consumed by the reaction to give D as fast as it is produced from A and that a steady state exists in which

$$\frac{dc_B}{dt} = 0$$

(7) Then, under this condition,

$$c_B = \frac{k_1 c_A}{k_1' c_C + k_2 c_A}$$

and

(8) $$\frac{dc_D}{dt} = k_2 c_A c_B = \frac{k_1 k_2 c_A^2}{k_1' c_C + k_2 c_A}$$

and, since 2 moles of A disappear for each mole of D produced,

(9) $$-\frac{dc_A}{dt} = \frac{2k_1 k_2 c_A^2}{k_1' c_C + k_2 c_A}$$

The rate of this reaction depends on the concentration of both A and C. When $k_2 c_A$ is small compared to $k_1' c_C$, the rate of change of the concentration of A depends on c_A^2, and the reaction is second order with respect to the reacting substance A; when $k_2 c_A$ is large compared to $k_1' c_C$, the rate depends on c_A, and the reaction is first order with respect to A.

In actual practice the exponent of c_A may shift gradually from first order through mixed orders to second order with respect to A as the reaction proceeds.

Determination of the Order of a Reaction. Simple examples have been given of clean-cut first-, second-, third-, and zero-order equations, but, as shown in the preceding section, it must not be supposed that all observed chemical reactions fit these types. The order of a reaction is determined by the exponents of concentration terms from which the rate of the reaction is determined. For example, in the reaction $A + B \rightarrow X$, the rate expression is

$$\frac{dc_X}{dt} = kc_A{}^m c_B{}^n \tag{28}$$

The rate of production of X depends on the concentration c of each of the materials taking part in the reaction each raised to an exponent which is determined empirically by experiment. Sometimes the exponents such as m and n are whole numbers, 1, 2, 3, etc., representing the number of moles of the material taking part stoichiometrically in the reaction. An example was given in equation 9. It is just as likely, however, that the experimental data will show that the rate of formation of X or the disappearance of A is given by an expression with fractional exponents such, for example, as

$$-\frac{dc_A}{dt} = kc_A{}^{1.3} c_B{}^1 \tag{29}$$

This situation emphasizes the fact that frequently there is little relation between the stoichiometrical reaction as written on paper and the order of the reaction as determined in the laboratory. In fact, most chemical reactions are complex, involving two or more different reactions or reaction steps going on simultaneously, although each of these intermediate reactions is likely to be a unimolecular or bimolecular reaction.

The sum of all the exponents involved in the rate equation is taken as the order of the reaction. Thus, in equation 9 it is second order, in equation 17 it is third order, and in equation 29 it is 2.3 order. There are several different ways in which the order of a reaction may be determined.

Substitution into Formulas. If a reaction is of first, second, third, or zero order, a constant value of k will be obtained throughout the course of the reaction when the data are substituted into the proper formula. If none of the formulas can be made to fit, the reaction is complicated, and probably two or more reactions are going on simultaneously.

Graphing. The order may sometimes be determined by plotting different functions of the concentration c against the time. If a straight line is obtained when $\log c$ is plotted against time, the reaction is first order as shown in equation 2.

In the special case where all the reactants have the same initial concentration, the reaction is second order if a straight line is obtained when $1/c$ is plotted against time, as shown in equation 12, and third order if a straight line is obtained when $1/c^2$ is plotted against time as shown in equation 17.

In a zero-order reaction a straight line is obtained when c is plotted against time as is evident from equation 20.

Half-Life Periods. In a first-order reaction the period of half-life (or in fact the time required for any given fraction to react) is independent of the initial concentration as shown in equation 8.

In a second-order reaction in which $a = b$, the time required for a given fraction to react is inversely proportional to the initial concentration, and $t_{1/2} = 1/ka$, as shown in equation 13.

Variation in Ratio of Reactants. When different molecules are involved, the course of the reaction may be studied by altering the ratio of the reacting materials. For example, the oxidation of nitric oxide,

$$2NO + O_2 \rightarrow 2NO_2$$

is accelerated more by increasing the concentration of nitric oxide than by increasing the concentration of oxygen. This fact is in accord with the equation:

$$\frac{dc_{NO_2}}{dt} = kc_{NO}{}^2 \times c_{O_2}$$

Much information may be gained in a complex reaction by increasing greatly the concentration of the reactants, one at a time, and observing the change in the reaction rate over a short period of time (for example, a period in which the change in composition is not over 10 per cent). Since

$$\frac{dx}{dt} = kc_A{}^m \cdot c_B{}^n \cdot c_C{}^j$$

where A, B, and C represent the different molecules reacting and m, n, j are the corresponding exponents in the rate equation, it is seen that m can be evaluated by doubling c_A, keeping c_B and c_C constant, and determining $\Delta x/\Delta t$ experimentally in the two cases. Thus, for short intervals where $(\Delta x/\Delta t)_{2c_A}$ is the observed rate when the concentration of A is doubled, giving $2c_A$ instead of c_A,

$$\frac{\left(\frac{\Delta x}{\Delta t}\right)_{2c_A}}{\left(\frac{\Delta x}{\Delta t}\right)_{c_A}} = \frac{k2^m c_A{}^m c_B{}^n c_C{}^j}{kc_A{}^m c_B{}^n c_C{}^j} = 2^m$$

Example 7. The chemical equation for the reaction between potassium oxalate and mercuric chloride is

$$2HgCl_2 + K_2C_2O_4 = 2KCl + 2CO_2 + Hg_2Cl_2$$

The weight of Hg_2Cl_2 precipitated from different solutions in a given time, at 100°, was as follows:

	$HgCl_2$ (moles per liter)	$K_2C_2O_4$ (moles per liter)	Time, minutes	Moles of Hg_2Cl_2 precipitated
(1)	0.0836	0.404	65	0.0068
(2)	0.0836	0.202	120	0.0031
(3)	0.0418	0.404	60	0.0032

Write the differential equation for the reaction rate, evaluating the exponents of the concentrations.

$$\frac{dx}{dt} = kc_{HgCl_2}{}^m c_{K_2C_2O_4}{}^n$$

From 1 and 2,

$$\frac{\left(\frac{\Delta x}{\Delta t}\right)_{2c_{K_2C_2O_4}}}{\left(\frac{\Delta x}{\Delta t}\right)_{c_{K_2C_2O_4}}} = \frac{\frac{0.0068}{65}}{\frac{0.0031}{120}} = 4 = \frac{k(c_{HgCl_2})^m(2c_{K_2C_2O_4})^n}{k(c_{HgCl_2})^m(c_{K_2C_2O_4})^n} = 2^n$$

Since $2^n = 4$, $n = 2$.

From 1 and 3,

$$\frac{\left(\frac{\Delta x}{\Delta t}\right)_{2c_{HgCl_2}}}{\left(\frac{\Delta x}{\Delta t}\right)_{c_{HgCl_2}}} = \frac{\frac{0.0068}{65}}{\frac{0.0032}{60}} = 2 = \frac{k(2c_{HgCl_2})^m(c_{K_2C_2O_4})^n}{k(c_{HgCl_2})^m(c_{K_2C_2O_4})^n} = 2^m$$

Since $2^m = 2$, $m = 1$.

Then,

$$\frac{dx}{dt} = kc_{HgCl_2}{}^1 c_{K_2C_2O_4}{}^2$$

It may be noted that the rate depends on the square of the potassium oxalate concentration, although the stoichiometric equation indicates that only one molecule is involved. Again, the reaction as written is bimolecular with respect to mercuric chloride but first order with respect to the concentration of mercuric chloride. These differences show that the reaction is complex and that the equation as written does not represent the full course of the reaction with its rate-determining intermediate steps.

Addition of Excess of Reactant. Often a complex reaction may be simplified and studied by adding a large excess of one or more of the re-

actants so that they do not undergo appreciable change during the reaction. If all but one of the reacting substances are present in large excess, a variation of the concentration of this one reactant permits a direct determination of the exponent to which the concentration of the reactant is raised in the rate equation.

Influence of Temperature. It has long been known as an empirical fact that many reactions in the neighborhood of room temperature approximately double or treble their velocity for a 10° rise.

A more quantitative relation, proposed by Arrhenius, is given in the following equation,

$$k = se^{-\Delta H_a/RT} \tag{30}$$

where s is a constant and ΔH_a is another constant, which is now interpreted as the heat of activation as explained on page 375. Set in logarithmic form,

$$\log k = \frac{-\Delta H_a}{2.303R}\frac{1}{T} + \text{constant} \tag{31}$$

Differentiating equation 31

$$\frac{d \ln k}{dT} = \frac{\Delta H_a}{RT^2} \tag{32}$$

and integrating between limits

$$\log \frac{k_2}{k_1} = \frac{\Delta H_a}{2.303R}\left(\frac{T_2 - T_1}{T_2 T_1}\right) \tag{33}$$

It may be noted that these equations are similar to those for equilibrium constants studied on page 282. According to equation 31, a straight line is produced when the logarithm of the specific reaction rate is plotted against the reciprocal of the absolute temperature. The specific decomposition rates of gaseous nitrogen pentoxide * at different temperatures are given in the third column of Table IV, and they are shown graphically in **Fig. 95.**

The slope of the line in Fig. 95 is -5400, and ΔH_a has the value of 24,700. Equation 31 becomes

$$\log k = -\frac{24{,}700}{2.303 \times 1.987}\frac{1}{T} + 13.638 \tag{34}$$

and equation 30

$$k = 4.3 \times 10^{13} e^{-24{,}700/1.987T}$$

* Daniels and Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921).

TABLE IV

DECOMPOSITION OF NITROGEN PENTOXIDE AT DIFFERENT TEMPERATURES

$t°$	$1/T$	$k_{obs.} \times 10^5$	$\log k$	$k_{calc.} \times 10^5$	Half-Life
65	0.002959	487	−2.313	477	2.38 min
55	0.003048	150	−2.824	155	7.72 min
45	0.003145	49.8	−3.303	47.2	21.8 min
35	0.003247	13.5	−3.871	13.2	85.9 min
25	0.003357	3.46	−4.471	(3.46) [1]	5.71 hours
0	0.003663	0.0787	−6.104	0.0733	10.2 days

[1] The value of $k_{obs.}$ at 25° was used for calculating $k_{calc.}$.

The calculated specific reaction rates when this formula is used are given in the fifth column of the table. The periods of half-life, calculated from the data in the third column, are given in the last column.

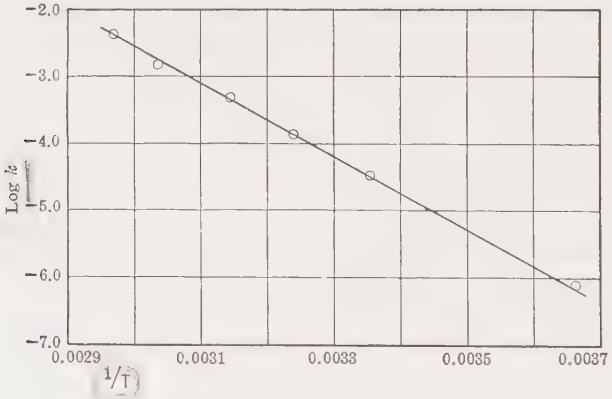


FIG. 95. Log k vs $1/T$ graph for the decomposition of N_2O_5 showing the method of determining activation energies.

The marked influence of temperature on reaction rates is clearly brought out in this table. Extrapolated values based on equation 34 are shown in Table V. It should be emphasized that the range between reactions which are too slow to measure and those which are too fast to measure is comparatively narrow. Ordinary laboratory measurements have usually been limited to the range between minutes and months.

TABLE V

Extrapolated Values of Half-Life

$t°$	Half-Life	$t°$	Half-Life
300	0.000039 sec.	25	5.7 hours
200	0.0039	0	11 days
150	0.088	−25	3 years
125	0.56	−50	830 years
100	4.6	−75	940,000 years
75	51	−100	8.4 billion years

A few other first-order gas reactions together with the Arrhenius constants are given in Table VI.

TABLE VI

First-Order Gas Phase Reactions

Decomposing Substance	Specific Reaction Rate, seconds^{-1}	Decomposing Substance	Specific Reaction Rate, seconds^{-1}
(1) N_2O_5	$k = 4.3 \times 10^{13}e^{-24,700/RT}$	(5) C_2H_5Br	$k = 3.8 \times 10^{14}e^{-54,800/RT}$
(2) SiH_4	$k = 2 \times 10^{13}e^{-51,700/RT}$	(6) $ClCO_2C_2H_5$	$k = 5.5 \times 10^{10}e^{-29,400/RT}$
(3) $Pb(C_2H_5)_4$	$k = 1.2 \times 10^{12}e^{-36,900/RT}$	(7) CH_3N_3	$k = 3 \times 10^{15}e^{-43,500/RT}$
(4) N_2O	$k = 4.2 \times 10^{9}e^{-53,000/RT}$	(8) Stilbene	$k = 6 \times 10^{12}e^{-42,800/RT}$

1. Daniels and Johnston, *J. Am. Chem. Soc.*, **43,** 53 (1921).
2. Hogness, Wilson, and Johnson, *J. Am. Chem. Soc.*, **58,** 108 (1936).
3. Leermakers, *J. Am. Chem. Soc.*, **55,** 4508 (1933).
4. Nagasako and Volmer, *Z. physik. Chem.*, **10B,** 414 (1930).
5. Vernon and Daniels, *J. Am. Chem. Soc.*, **55,** 922 (1933).
6. Choppin, Frediani, and Kirby, *J. Am. Chem. Soc.*, **61,** 3176 (1939).
7. Leermakers, *J. Am. Chem. Soc.*, **55,** 2719 (1933).
8. Isomerization of *cis*-stilbene, Kistiakowsky and Smith, *J. Am. Chem. Soc.*, **56,** 638 (1934).

Kinetic Theory of Gases. Information concerning the distribution of energy among molecules and the frequency of collisions may be obtained from the kinetic theory of gases. This, in turn, is valuable in the study of reaction rates.

The unordered motion of colloid particles can be directly observed under the microscope, as described on page 532, and we have every reason to believe that the motions of molecules in a gas are similar. A series of collisions in the right direction may give to a molecule an abnormally high velocity, and on the other hand a head-on collision may

completely stop a molecule for a brief interval of time. Since the velocities are determined by chance, and since a large number of molecules are involved in any measurement, the laws of probability may be applied with exactness.

The distribution of velocities is known as the Maxwell distribution law. It is illustrated * in **Fig. 96** for gaseous nitrogen pentoxide, which has a molecular weight of 108. It is seen that there is a most probable

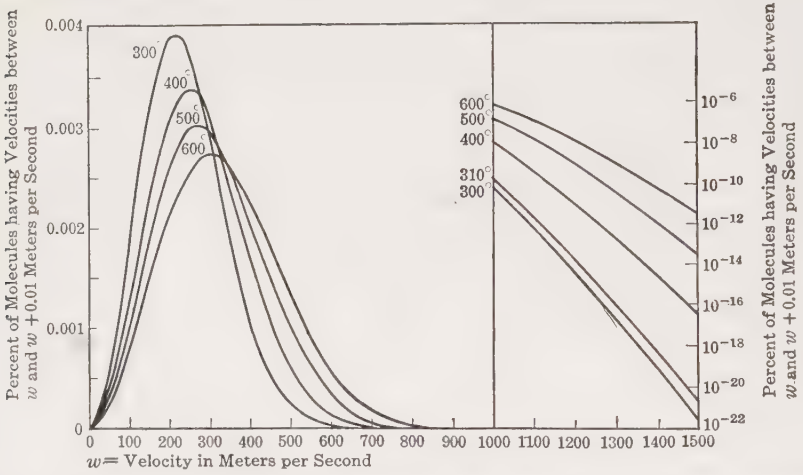


FIG. 96. Maxwell distribution of velocities in molecules (of N_2O_5) with enlarged scale of ordinates at the right for high velocities corresponding to activation energies of chemical significance. The ordinates at the right are plotted on a logarithmic scale.

velocity which varies with the temperature and that there are very few molecules with very high or very low velocities.

It is only the molecules which possess extremely high velocities that are of any interest in chemical reactions. For example, in nitrogen pentoxide an energy of 24,700 cal per mole, equivalent to a velocity of nearly 1400 m per second, is required for decomposition.

In other words, those molecules with velocities of about 1400 m per second or more have sufficient energy to undergo chemical reaction. The relative number of these "activated" molecules is exceedingly small at room temperature, and, hence, the reaction is slow. As shown by the exaggerated scale at the right, the number of these rapidly moving molecules is greatly increased by an increase in temperature.

* Calculated with the formula

$$\frac{dn}{n} = \frac{2}{\sqrt{\pi}} \left(\frac{1}{RT}\right)^{3/2} e^{-E/RT} E^{1/2}\, dE$$

given in the appendix, page 678.

An approximate derivation of the Maxwell law for the distribution of velocities among molecules can be obtained by calculating the probability that molecules will move with specified velocities in specified directions in a two-dimensional plane. Under these conditions it can be shown that

$$\frac{dn_E}{n} = \frac{1}{RT} e^{-E/RT}\, dE \tag{35}$$

where n is the total number of molecules and n_E is the number of molecules having kinetic energy of translation between E and dE. Integrating from E to infinity to determine the number of molecules with energies greater than E yields

$$\frac{1}{n}\int_E^\infty dn_E = \frac{1}{RT}\int_E^\infty e^{-E/RT}\, dE$$

$$\frac{n_E}{n} = e^{-E/RT} \tag{36}$$

where n_E/n is the fraction of the molecules having energies greater than E.

A more exact expression derived on the basis of the three axes instead of two (given in the appendix on page 678) is

$$\frac{n_E}{n} = \frac{2}{\sqrt{\pi}} e^{-E/RT}\left(\frac{E}{RT}\right)^{1/2} \tag{37}$$

Example 8. Calculate at 25° and at 35° the fraction of nitrogen pentoxide molecules having a kinetic energy equal to or greater than 24,700 cal per mole and the effect of a 10° rise in temperature on this fraction.

At 25° $$\frac{n_E}{n} = \frac{2}{\sqrt{\pi}} e^{-E/RT}\sqrt{\frac{E}{RT}} = \frac{2}{\sqrt{\pi}} e^{-24{,}700/(1.987\times 298.1)}\sqrt{\frac{24{,}700}{1.987\times 298.1}}$$

$$= 5.69 \times 10^{-18}$$

At 35° $$\frac{n_E}{n} = \frac{2}{\sqrt{\pi}} e^{-24{,}700/(1.987\times 308.1)}\sqrt{\frac{24{,}700}{1.987\times 308.1}} = 2.17 \times 10^{-17}$$

$$\frac{(n_E/n)_{35^\circ}}{(n_E/n)_{25^\circ}} = \frac{2.17\times 10^{-17}}{5.69\times 10^{-18}} = 3.81$$

This ratio of 3.8 in the fraction of activated molecules is in close agreement with the ratios of the reaction rates at 35° and 25° as given in Table IV,

$$\frac{13.2\times 10^5}{3.46\times 10^5} = 3.82$$

indicating that the major increase in the reaction rate is due to an increase in the

fraction of activated molecules. It should be emphasized that the total kinetic energy of the gas, $\frac{3}{2}RT$, increases only 3.3 per cent when the temperature is raised from 298.1 to 308.1. Most of this energy, however, is too low to do anything chemically. Only kinetic energy of 24,700 cal per mole or greater is effective in bringing about this reaction, and this high-intensity energy is increased greatly by a 10° rise, as shown.

Molecular Collisions in Gases. Four quantities of use in chemical kinetics may be calculated from the kinetic theory of gases introduced in Chapter II. They are: (1) the number of molecules striking a surface, (2) the number of collisions per second between molecules in a gas, (3) the molecular diameters, and (4) the distance a molecule travels before colliding with another molecule.

1. Number of Molecules Striking a Surface. If n molecules are contained in a cube 1 cm on an edge, it may be assumed that one sixth of them are moving toward one wall. The root-mean-square velocity is u centimeters per second, and the number of molecules hitting the wall in a second will be equal to one sixth of the number which are within a distance of u centimeters from it. Even if one of these molecules is prevented from hitting the wall by colliding with another molecule, the second molecule will be deflected back so that the number of hits is the same. If there are n molecules in the 1-cm cube, the number hitting one wall (1 sq cm) is $\frac{1}{6}nu$ (1^2). A closer analysis which allows for unequal speeds and collisions at oblique angles gives $1/\sqrt{6\pi}$ or 0.230 instead of 1/6. Then,

$$\text{Collisions per square centimeter of wall per second} = 0.230nu \quad (38)$$

It was shown on page 28 that

$$u = \sqrt{\frac{3RT}{M}} \quad (39)$$

Since u is expressed in centimeters per second, R must be expressed in ergs per degree to keep both in cgs units.

2. Frequency of Collisions. A rough idea of the number of collisions between molecules may be obtained from the following considerations. If the diameter of a molecule is σ, and two molecules are just touching, the distance separating their centers is also σ. If molecules are considered to be points, each molecule can collide with all other molecules which come within the distance σ from its center. A molecule moving with a velocity of u centimeters per second will sweep out during a second a cylindrical space u centimeters long with an *effective* cross section $\pi\sigma^2$. The cylindrical space may be zigzag in shape on account

of deflections suffered during collisions. If there are n molecules per cubic centimeter, this molecule will collide with $(\pi u\sigma^2)n$ other molecules, but each of the n molecules will sweep out this effective volume and undergo the same number of collisions. The total number of molecules undergoing collisions is therefore $(\pi u\sigma^2 n)n$. Certain approximations are involved in this derivation, and, when corrections are made for the distribution of velocities and other factors, the number of molecules colliding is given more exactly by the expression:

$$\tfrac{4}{3}\sqrt{(3\pi)}u\sigma^2n^2 \quad \text{or} \quad 4.09u\sigma^2n^2$$

The number of collisions is one-half the number of molecules colliding, because two molecules are necessary for a collision. The number of collisions z per second per milliliter is given by the equation:

$$z = 2.05u\sigma^2n^2 \tag{40}$$

By substituting for u its equivalent given in equation 39 and combining and rounding off numbers, the following approximate equation is obtained:

$$z = 3.54\sigma^2n^2\sqrt{\frac{RT}{M}} \tag{41}$$

3. Molecular Diameters. All the quantities necessary for calculating the frequency of collisions are readily obtainable, except the molecular diameter σ. This quantity can be calculated from viscosity measurements, similar to those described for liquids on page 187. A few values are given in Table VII.

TABLE VII

Molecular Diameters (σ)

Gas	σ	Gas	σ
Helium	2.18×10^{-8} cm	Hydrochloric acid	2.86×10^{-8} cm
Argon	3.36	Hydrobromic acid	3.16
Chlorine	4.96	Hydriodic acid	3.50
Bromine	3.42	Carbon dioxide	4.18
Iodine	3.96	Hydrogen	2.47
Oxygen	3.39	Nitrogen pentoxide	8.53
Nitrogen	3.50		

Many of the diameters calculated from viscosity measurements are in close agreement with the diameters as calculated from X-ray meas.

urements on crystals, and there is good evidence that the diameters of most molecules are of the order of 10^{-8} cm or perhaps 2 to 10A. In fact, when no data are available, it may be assumed for the purpose of estimating the number of collisions that the molecular diameter is 5×10^{-8} cm. In certain phenomena involving radiation, however, molecules appear to have effective diameters which are much larger.

4. Mean Free Path. If a molecule travels u centimeters in a second and collides with $\pi u\sigma^2 n$ molecules per second, as shown before, the average distance between encounters l, called the mean free path, is given by the equation:

$$l = \frac{u}{\pi u\sigma^2 n} = \frac{1}{\pi\sigma^2 n}$$

Closer analysis shows that

$$l = \frac{1}{\sqrt{2}\pi\sigma^2 n} \tag{42}$$

A knowledge of the mean free path is useful in calculations involving collisions in chemical reactions and rates of diffusion of gases. In all these formulas, 38, 39, 40, 41, and 42, the velocities u are given as the root-mean-square velocities. The average velocities and the most probable velocities vary slightly from these values.

Example 9. Nitrogen is contained in a vessel at 1 atm pressure at 25°. Calculate: (*a*) the number of collisions on the walls per second per square centimeter; (*b*) the number of collisions between molecules per second per milliliter; (*c*) the mean free path.

It is necessary first to calculate the number of molecules n per milliliter and the velocity of the molecules u,

$$n = 6.02 \times \frac{10^{23}}{\left(22{,}400 \times \frac{298.1}{273.1}\right)} = 2.46 \times 10^{19}$$

$$u = \sqrt{\frac{3RT}{M}} = \left(\frac{3 \times 8.314 \times 10^7 \times 298.1}{28}\right)^{1/2} = \sqrt{26.56 \times 10^8}$$

$$= 5.15 \times 10^4 \text{ cm sec}^{-1}$$

(*a*) $0.230nu = 0.230 \times 2.46 \times 10^{19} \times 5.15 \times 10^4$
$= 2.92 \times 10^{23}$ collisions cm^{-2} sec^{-1}

(*b*) $2.05u\sigma^2 n^2 = 2.05 \times 5.15 \times 10^4 \times (3.50 \times 10^{-8})^2 \times (2.46 \times 10^{19})^2$
$= 7.83 \times 10^{28}$ collisions between molecules cm^{-3} sec^{-1}

(*c*) $l = \dfrac{1}{\sqrt{2}\pi\sigma^2 n} = \dfrac{1}{1.41 \times 3.14 \times (3.50 \times 10^{-8})^2 \times 2.46 \times 10^{19}}$

$= 7.47 \times 10^{-6}$ cm = the mean free path

Activation of Molecules. According to present theories, it is necessary for molecules to become activated before they can react. If all molecules were equally reactive, it would be difficult to account for the very existence of slow reactions. Since the number of collisions per second is enormous, it might be expected that all reactions would be instantaneous. Ionic reactions, such as neutralizations and precipitations, are, in fact, immeasurably fast, but the energy of activation required for ions to react is usually very small.

Chemical equilibria and thermodynamics involve only the initial and final states, and they are not concerned with the mechanisms of the reaction nor with the intermediate steps. In chemical kinetics, however, we are interested in the reaction steps which lead to the final products, and we try to apply our thermodynamical calculations not to the whole reaction but to the activation process.

Thus, in the over-all reaction,

$$\text{Reactants} \rightarrow \text{products} \quad \text{or} \quad A \rightarrow C$$

we are concerned with ΔH, which is equal to $H_{\text{products}} - H_{\text{reactants}}$, but, in chemical kinetics, the same reaction is written

$$\text{Reactants} \xrightarrow[\text{slow}]{} \text{activated molecules} \xrightarrow[\text{fast}]{} \text{products}$$

or

$$A \rightarrow B \rightarrow C$$

and we are concerned with the slow or rate-determining step for which

$$\Delta H_a = H_{\text{activated molecules}} - H_{\text{reactants}}$$

For the reverse reaction $C \rightarrow B$, $\Delta H_a' = H_{\text{activated molecules}} - H_{\text{products}}$

The relation between the heat of reaction and the heats of activation is given in **Fig. 97.**

The initial molecules A require the absorption of a definite amount of heat ΔH_a in order to put them in an activated state B from which they can rearrange to give the products C. In order to reverse the reaction, the molecules C must be supplied with the heat of activation $\Delta H_a'$, and, therefore, in passing from the activated state B, to C, an amount of heat equal to $\Delta H_a'$ is evolved. The heat of reaction measured in a calorimeter at constant

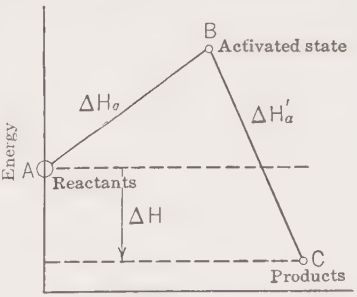


FIG. 97. Relation between activation energy of forward and reverse reactions and the heat of reaction.

pressure is equal to the difference between the heat of activation in the two directions.

$$\Delta H = \Delta H_a - \Delta H_a' \tag{43}$$

Usually the heat evolved in the step BC is greater than the heat absorbed in the step AB, and the over-all reaction in going from A to C is an evolution of heat. If ΔH_a happens to be greater than $\Delta H_a'$, the reaction is endothermic.

It may be remembered that, if the reaction is carried out at constant volume instead of constant pressure, the heat of reaction is ΔE rather than ΔH. The two are practically the same in solutions, where there is but little change in volume, and even in gaseous reactions involving a change in volume the difference is usually small in comparison with the values of ΔH.

The energy required for the activated state is the chief factor in determining the speed of the reaction. It was shown that, the greater the energy required for activation, the fewer are the molecules possessing this energy; and, hence, the slower is the reaction at a given temperature. The heat of reaction ΔH is of no significance for calculating reaction rates. As Hinshelwood has suggested, there is no more connection between the heat of reaction and the energy of activation than there is between the difference in levels of two valleys and the height of a mountain pass which separates them.

One very useful generalization can be made, however. In endothermic reactions, the energy required for activation must be at least as great as the endothermic heat of reaction. This is equivalent to saying that in going from a lower to a higher valley the route must traverse an elevation at least as high as the upper valley. Often it is difficult to calculate the energy of activation, but, if the reaction is endothermic, the heat of reaction may be used as a *minimum* value.

Example 10. The heat of combustion of a carbohydrate is 112,000 cal per mole of carbon. To effect the reverse reaction, namely, the combination of carbon dioxide and water to form a carbohydrate, what is the minimum activation energy required?

Since this reverse reaction is endothermic by 112,000 cal, an activation energy of at least 112,000 cal must be supplied. It is quite possible that more than 112,000 cal will be necessary.

The heat of activation ΔH_a cannot be measured calorimetrically, because the activated molecules have only a brief existence. It is determined indirectly by plotting $\log k$ against $1/T$ and multiplying the slope by $2.303R$ just as heat of reaction is determined by plotting $\log K$ against $1/T$, where K is the equilibrium constant (page 282). In this

way the heat of activation was found, on page 365, to be 24,700 cal per mole for the decomposition of nitrogen pentoxide.

Example 11. Combining equations 32 and 43, show that the Arrhenius equation can be used to derive the known relation between equilibrium constants and heat of reaction.

$$\frac{d \ln k}{dT} = \frac{\Delta H_a}{RT^2} \quad \text{and} \quad \frac{d \ln k'}{dT} = \frac{\Delta H_a'}{RT^2}$$

where k and ΔH_a refer to the forward reaction and k' and $\Delta H_a'$ refer to the reverse reaction.

Subtracting gives

$$\frac{d(\ln k - \ln k')}{dT} = \frac{\Delta H_a - \Delta H_a'}{RT^2}$$

$\Delta H = \Delta H_a - \Delta H_a'$, and, from page 255, $k/k' = K$. Then,

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

This relation was proved by thermodynamics on page 280, thus lending support to the validity of the Arrhenius equation.

The Arrhenius Equation. The considerations just discussed apply to free energy as well as to enthalpy, and

$$\Delta F = \Delta F_a - \Delta F_a' \tag{44}$$

It is now worth while to examine more fully the Arrhenius equation,

$$k = se^{-\Delta H_a/RT}$$

and to interpret the constants in terms of physical-chemical concepts. Since ΔH_a and RT are expressed in the same units, usually calories, $e^{-\Delta H_a/RT}$ is dimensionless. Then s has the same dimensions as k and, for first-order reactions, involves a number per second.

The rate of the over-all reaction depends on the concentration of the activated molecules, and this concentration may be calculated with the help of thermodynamical relations. There is an equilibrium between reacting and activated molecules, and

$$K_a = \frac{c_{\text{activated}}}{c_{\text{reactant}}}$$

It will be remembered (pages 150 and 269) that

$$\Delta F = \Delta H - T\,\Delta S$$

and that

$$\Delta F^0 = -RT \ln K$$

Then,

$$K_a = e^{-\Delta F_a{}^0/RT} = e^{\Delta S_a/R} e^{-\Delta H_a/RT} \tag{45}$$

There are complications involved in calculating the concentration of the activated molecules from this equilibrium constant and the concentration of the reactants. The more complete rate equation is derived in part in the appendix on page 679. It is

$$k = \frac{RT}{Nh} e^{\Delta S_a/R} e^{-\Delta H_a/RT} \tag{46}$$

where N is Avogadro's constant and h is Planck's constant, 6.6×10^{-27} (page 570). This is the fundamental equation of Eyring's theory of the "activated complex." For a complete interpretation the literature must be consulted.*

This equation constitutes the proof, promised earlier, that the constant ΔH_a in the Arrhenius equation is the *heat of activation*. Moreover, it is evident that the factor s in the Arrhenius equation, known as the frequency factor, has the following significance:

$$s = \frac{RT}{Nh} e^{\Delta S_a/R} \tag{47}$$

At ordinary temperatures the term RT/Nh is about $(8.3 \times 10^7 \times 300) \div (6.0 \times 10^{23} \times 6.6 \times 10^{-27})$ or 10^{13}. This is the same order of magnitude as the frequency in the infrared spectrum (page 595) which is due to the natural vibration period of atoms within the molecule. The term $e^{\Delta S_a/R}$ is an entropy term, and for unimolecular reactions it may often be taken as unity in gas reactions, because the activated complex is so much like the original reactants that the entropy change is very small. In some reactions, however, particularly in certain rearrangements and in bimolecular reactions, the entropy of activation may become fairly large, and, thus, the frequency factor may become important in determining the reaction rate. In a series of related compounds the influence of structure on the reaction rate is sometimes a matter of changes produced in the entropy of activation. It must be remembered that these activated molecules or the activated complex have only a transitory existence and that it will probably never be possible to isolate them and make measurements on them. The value of ΔS_a must be determined by indirect methods.

In many bimolecular reactions the frequency factor s turns out to be approximately equal to the number of molecules colliding, per unit volume and time, when at unit concentration. As a first approximation in such cases, it may be supposed that the rate of reaction is determined

* Eyring, *J. Chem. Phys.*, **3**, 107 (1935); Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, 1941.

by the rate at which *activated* molecules collide and give the products of the bimolecular reaction. On this hypothesis it is proportional to the number of molecules colliding multiplied by $e^{-\Delta H_a/RT}$, which is approximately equal to the fraction of molecules in the activated state. But there are many bimolecular reactions, particularly in solution, in which the reaction goes much more slowly than predicted by this formula. It has been customary to assume that a certain orientation at the time of collision, a type of lock-and-key effect, is necessary for complete reaction. The more exact statistical development giving $(RT/Nh)e^{\Delta S_a/R}$ for the frequency factor leads to terms which are approximately equivalent to the product of the collision frequency and the orientation factor.

Example 12. In the bimolecular decomposition of gaseous hydrogen iodide the heat of activation has been found by equation 33 to be 45,600 cal. Then, at 393.7°, from equation 37,

$$\frac{n'}{n} = \frac{2}{\sqrt{\pi}} e^{-\Delta H_a/RT} \sqrt{\frac{\Delta H_a}{RT}} = 7.3 \times 10^{-15}$$

If the concentration of hydrogen iodide is 1 mole per liter, the number of molecules colliding per milliliter per sec is given by the expression:

$$\begin{aligned} 2z &= 2 \times 3.54\sigma^2 n^2 \sqrt{\frac{RT}{M}} \\ &= 2 \times 3.54 \times (3.5 \times 10^{-8})^2 \times \left(\frac{6.02 \times 10^{23}}{1000}\right)^2 \times \sqrt{\frac{8.3 \times 10^7 \times 666.8}{127.9}} \\ &= 6.6 \times 10^{31} \end{aligned}$$

Expressed in terms of moles colliding per second per liter,

$$2z = 6.6 \times 10^{31} \times \frac{1000}{6.02 \times 10^{23}} = 1.1 \times 10^{11}$$

Then calculating the number of moles activated at 393.7°, we have

$$k = 2z \times \frac{n'}{n} = 1.1 \times 10^{11} \times 7.3 \times 10^{-15} = 8.0 \times 10^{-4}$$

The experimentally determined value is 2.6×10^{-4} mole $^{-1}$ liter. This fair agreement shows that there is no large orientation effect in this simple reaction.

The Prediction of Reaction Rates. The Arrhenius equation is found to fit the rate measurements on a surprisingly large number of different reactions at various temperatures. If the heat of activation is known from experimental measurements, or if it can be estimated from theoretical considerations (page 694), it is possible to predict the reaction-rate constant at any temperature, provided an approximate value can

be assigned to the frequency factor. Because of the exponential character of the equation, it is more important in calculating the rate constant k to know the heat of activation accurately than to know the frequency factor with precision.

From what has been said in the preceding section, it is evident that for many unimolecular gas reactions the entropy of activation is small, and the following relation holds approximately:

$$k = 10^{13} e^{-\Delta H_a/RT} \tag{48}$$

In a critical survey * of 28 of the best examples of unimolecular gas-phase reactions reported in the literature from 1936–41, the value of s in the Arrhenius equation was found to be between 10^{12} and 10^{14} in 60 per cent of the reactions.

On the basis of these facts the chart of **Fig. 98** is useful in predicting reaction rates for many gas-phase unimolecular decompositions.

The values of k in sec^{-1} on the slanting lines are recorded at the right. It is a simple matter to obtain a rough estimate of k by graphical interpolation. The situation is simplified by the fact that very rapid or very slow reactions are of no practical concern, the ordinary time of observation of the course of a reaction being not less than a few seconds nor more than a few months. The values of k falling within this time range are roughly from 10^{-1} to 10^{-7} sec^{-1}.

The prediction of reaction rates is simplified also by the fact that the range of activation energies is limited very roughly to the range 10,000 to 100,000 cal per mole. Very few chemical reactions require more than 100,000 cal per mole of activation energy, and the ones with less than 10,000 cal are usually too fast to measure. A very large number of activation energies range from 15,000 to 60,000 cal.

If the energy of activation for a first-order reaction is 25,000 cal per mole and the temperature is 300° K (a little over room temperature), k has a value of 10^{-5}, if it is assumed that s has a value of 10^{13}. When k is 10^{-5}, the period of half-life is about 19 hours. These data fit the case of nitrogen pentoxide fairly well.

Again, the energy of activation for the first-order decomposition of ethyl bromide is about 55,000 cal per mole, and it is evident that the temperature must be above 650° K to give appreciable decomposition. As another illustration, it may be concluded that at 500° K one is concerned in unimolecular reactions only with those reactions that have values of ΔH_a between 25,000 and 45,000 cal per mole. With larger values of ΔH_a the reaction is too slow to measure; with smaller values it is too fast.

* Daniels, Prediction of Reaction Rates, *Ind. Eng. Chem.*, **35**, 514 (1943).

The chart may be used as a rough estimate in many reactions, but large errors are more likely to be made if it is used for unimolecular reactions in solutions. In bimolecular reactions it was seen that part of the frequency factor may be interpreted as the number of collisions.

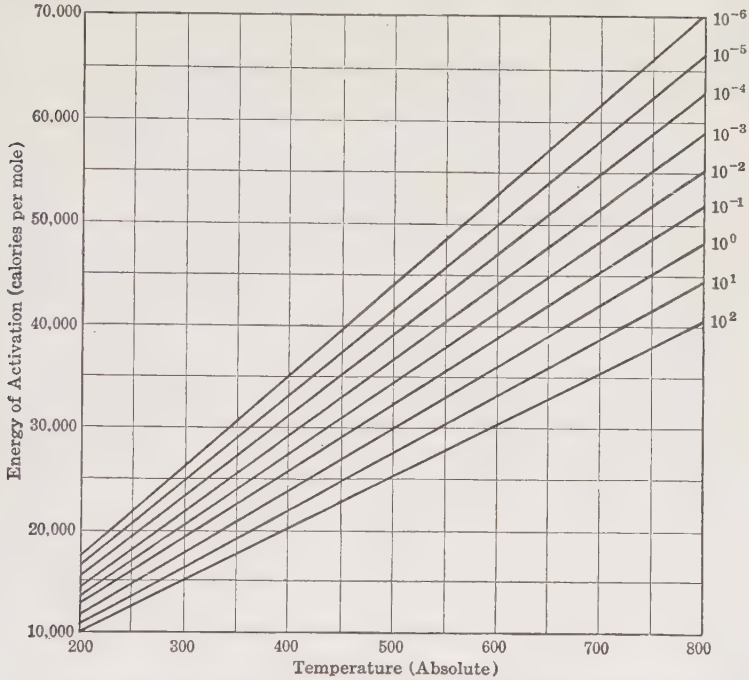


FIG. 98. Chart for predicting specific reaction rates at different temperatures for different activation energies, if a frequency factor of 10^{13} is assumed.

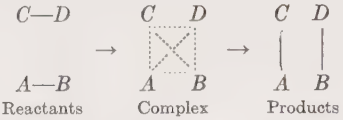
These depend on molecular weights and other factors, but, when they are expressed in moles per liter, they have a value ranging around 10^{10}. In bimolecular reactions, then, the expression,

$$k = 10^{10} e^{-\Delta H_a/RT}$$

offers a possible but still more unsatisfactory means for predicting reaction rates. The entropy of activation or the orientation factor is likely to cause large departures from this estimate.

The prediction of activation energies from known physical-chemical constants would be highly desirable. As stated already, the heat of reaction cannot be used as an indication of the activation energy. An upper limit of the activation energy might be taken as the energy required to pull the reactants completely apart to give isolated atoms as calculated by adding up the heats of dissociation of the bonds broken

(page 134). Certainly, they would then be in an activated state ready to react, but usually the activation can be accomplished with a lesser expenditure of energy. If there is only an instantaneous collision and separation, the energy evolved by the formation of the new bonds is dissipated by collision to the surrounding molecules and cannot be used in appreciable amounts to activate the reacting molecules. However, some of the energy of new bond formation can be used if a complex is formed. Thus



The energy of activation must be somewhere between the heat of reaction and the energy required to produce separated atoms. One approach to the calculation is given on page 694. According to another very simple approach, the activation energy for a bimolecular reaction is taken as 28 per cent of the energy required to dissociate the molecules into atoms or groups of atoms, that is, the sum of the dissociation energies of the bonds broken. Hirschfelder * arrived at this empirical rule by finding that, in the case of the decomposition of hydrogen iodide gas, which is one of our most accurately known reactions, the experimentally determined activation energy is 28 per cent of the energy required to dissociate HI into hydrogen and iodine atoms. He then assumed that this 28 per cent is a general constant applicable to other bimolecular reactions. The rule seems to hold quite well, but the number of cases where experimental checks are possible is quite limited.

Example 13. Estimate the activation energy for the reaction:

$$2ICl\ (g) + H_2\ (g) = 2HCl\ (g) + I_2\ (g)$$

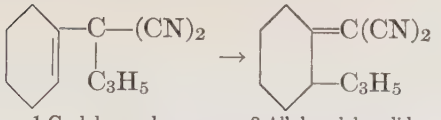
For $ICl \rightarrow I + Cl$, $\Delta H = 50{,}800$, and, for $H_2 \rightarrow 2H$, $\Delta H = 97{,}000$.

Then $\Delta H_a = 0.28(50{,}800 + 97{,}000) = 41{,}300$. The experimentally determined value of ΔH_a calculated from kinetic data is 34,000 cal per mole.

Entropy of Activation. Although the entropy of activation is small, as already explained, in most unimolecular reactions which involve merely the rupture of bond, it may not be small in unimolecular reactions which involve a molecular rearrangement, particularly if the formation of the activated complex involves a complicated or improbable shape. An example is the rearrangement of 1-cyclohexenyl allylmalonitrile † according to the reaction:

* Hirschfelder, *J. Chem. Phys.*, **9**, 645 (1941).

† Foster, Cope and Daniels, *J. Am. Chem. Soc.*, **69**, 1893 (1947).



1-Cyclohexenyl allylmalonitrile → 2-Allyl cyclohexylidene malonitrile

The rate of the reaction was followed by measuring the refractive index at successive times, and the concentration of 1-cyclohexenyl

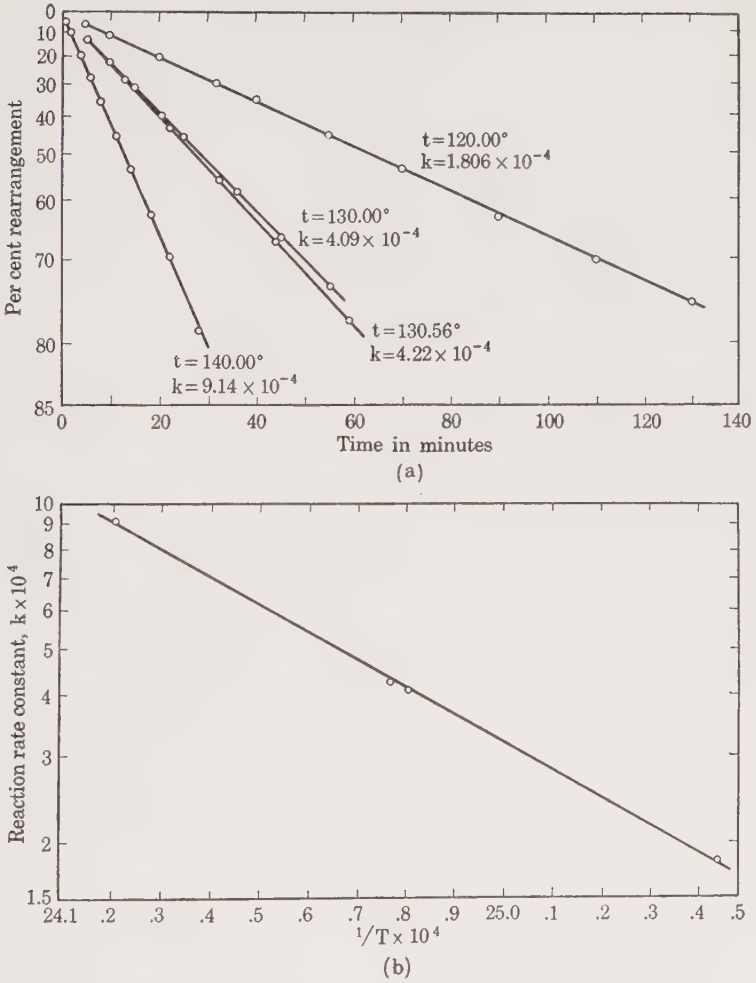


FIG. 99. Rates and activation energy for the rearrangement of 1-cyclohexenyl allyl malonitrile.

allylmalonitrile is plotted on a logarithmic scale against the time at different temperatures in **Fig. 99*a***. The rate constants are calculated from

the slopes of these lines, and in **Fig. 99*b*** the specific rate constants are plotted on a logarithmic scale against the reciprocal of the absolute temperature to obtain the activation energy. ΔH_a is 26,160 cal. In the Eyring equation,

$$k = \frac{RT}{Nh} e^{\Delta S_a/R} e^{-\Delta H_a/RT}$$

All the quantities have been evaluated except ΔS_a, the entropy of activation. When this equation is solved, ΔS_a is found to be -9.9 entropy units. This fairly large entropy of activation suggests the formation of a distorted ring structure for the activated complex which then breaks up in such a way that the C_3H_5 group becomes attached to the cyclohexenyl group.

The rate equation then at 130° is

$$k = \frac{RT}{Nh} e^{\Delta S_a/R} e^{-\Delta H_a/RT}$$

$$= \frac{8.31 \times 10^7 \times 403}{6.02 \times 10^{23} \times 6.62 \times 10^{-27}} e^{-9.9/1.99} e^{-26{,}160/(1.99 \times 403)}$$

$$= 5.85 \times 10^{10} e^{-26{,}160/(1.99 \times 403)} = 0.00040 \text{ sec}^{-1}$$

Catalysis. A substance which increases the rate of a chemical reaction without being used up in the reaction is called a *catalyst.* There are many different kinds of catalysts and many different mechanisms by which the catalyst operates.

The function of the catalyst is to bring about the desired reaction with a smaller heat of activation. A lower heat of activation gives a more rapid reaction because more molecules have the required amount of energy to react. The high energy requirement is avoided by some bypass. Usually the by-passing consists in forming a new compound with less energy consumption and then decomposing this intermediate compound in such a way as to regenerate the catalyst. In this way the catalyst is used over and over again.

Thus, if a reaction represented by the equation,

$$A + G = AG$$

takes place very slowly under ordinary conditions, it is possible to increase its velocity by the addition of an appropriate catalyst H. Then

$$(1) \quad A + H = AH$$

$$(2) \quad AH + G = AG + H$$

The catalytic action of nitrogen dioxide in the oxidation of sulfur dioxide offers a good example. The rate of the reaction represented by the equation

$$2SO_2 + O_2 = 2SO_3$$

is very small. The accelerating action of nitric oxide on the reaction may be represented in the following simplified manner:

$$(1) \quad 2NO + O_2 = 2NO_2$$

$$(2) \quad 2SO_2 + 2NO_2 = 2SO_3 + 2NO$$

$$(3) \quad 2NO + O_2 = 2NO_2, \text{ etc.}$$

There are many examples in organic chemistry in which the catalyst accelerates the reaction by forming an intermediate compound which reacts faster than the original reactants. One of the earliest examples was discovered when ethyl sulfate was detected in the reaction of alcohol to give ether using sulfuric acid as a catalyst. Another important example is the catalytic action of aluminum chloride in the well-known Friedel-Crafts synthesis of organic compounds which has been shown to involve the formation of an additional compound.

It must be emphasized that the conditions for catalysis are rather specific. If the intermediate compound is too unstable, it cannot act catalytically; if it is too stable, no further reaction is possible. It must have just the right degree of stability.

The catalyst accelerates the reverse reaction to the same extent as the forward reaction so that their ratio, the equilibrium constant, is unaffected.

Sometimes the catalyst may *appear* to change the equilibrium but in such cases large quantities of the catalyst are usually required and the material not only accelerates the reaction but also changes the effective concentrations of the reacting materials. Changing the solvent, for example, may accelerate a reaction, and it may also change the equilibrium, but the two effects are entirely independent. The catalytic effect is not responsible for the equilibrium shift.

Sometimes one of the products of reaction functions as a catalyst. Such a substance is called an autocatalyst. Normally, of course, the reaction rate decreases continually, but in autocatalytic reactions the rate increases to a maximum and then decreases.

Contact Catalysis. The phenomenon of adsorption is discussed on page 547 where it is seen that in many cases the surface of a solid may be regarded as a checkerboard of atoms on which molecules from the gas phase, or from solution, become attached. The adsorbed layer is

then limited to a thickness of 1 molecule. There may be further condensation of easily liquefiable gases in the minute capillaries of substances like charcoal and silica gel, but this phenomenon is not ordinarily involved in catalysis.

When molecules are adsorbed at a surface, the energy content is altered, and there is opportunity for forming new products. Adsorption does not necessarily produce catalytic reactions, but catalytic reactions at surfaces generally involve adsorption. Apparently some atoms at the surface are in better position to bring about reaction than others. Moreover, the exact spacing between atoms in the lattice of the catalyst is important, and this distance can be altered by changing the method of preparation and adding extra substances.

The rate of a reaction catalyzed by a surface depends to a large extent on the fraction of the surface which is covered with adsorbed gas. When the surface is nearly bare, the pressure of the gas determines the extent of adsorption, and this, in turn, determines the rate of the reaction. Since the reaction rate is proportional to the concentration of the gas, the reaction follows the first-order equation. When the surface remains practically saturated, on the other hand, the pressure of the gas has no influence on the reaction rate, and the reaction is of the zero order. When ammonia is decomposed on a tungsten filament, for example, the rate of decomposition is independent of the pressure, over a wide range of pressure.

When the surface is partly covered, the reaction rate is proportional to something between p^1 and p^0, namely, to p^n, where p is the pressure of gas and n is some fractional number which is determined empirically by experiment.

The activity of a catalyst is altered appreciably by extremely minute amounts of foreign substances. Foreign substances which tend to inhibit catalytic activity are known as *poisons;* substances which tend to enhance the activity are known as *promoters.* It is easy to see how a small number of molecules can react permanently with the few atoms at the surface to destroy the catalytic properties. For example, in the manufacture of sulfuric acid by the contact process, the presence of a very minute amount of arsenic completely destroys the catalytic activity of the platinum catalyst by forming platinum arsenide at the surface. Certain metals and metallic oxides act as promoters in some cases by rendering the catalyst less susceptible to poisoning, but in many cases they act by increasing the interfaces at which loose adsorption compounds are formed, having just the right degree of stability to produce a rapid catalytic reaction.

The catalytic activity of the walls of the containing vessel is a factor

in many gaseous reactions. The thermal decomposition of organic materials frequently occurs on the walls. In such cases the temperature coefficient is usually small, because the slowest process is the diffusion of the products away from the walls, and a diffusion process is subject only to the simple laws of the kinetic theory of gases. A 10° rise at about 300° K increases the diffusion rate by only about 3 per cent, whereas a chemical reaction is normally increased about 300 per cent, as already explained.

A wall effect may be distinguished from a homogeneous gas reaction by (1) the temperature coefficient, (2) increasing the area greatly, as by adding powdered glass to a glass vessel, (3) changing the nature of the vessel walls. Quartz may be used instead of glass, for example, or the walls may be coated. The reaction between bromine and ethylene is a wall effect, as shown by the fact that the reaction is stopped when the glass walls are covered with paraffin. When glass vessels are coated with the new water-repellent silicones, the character of some gaseous reactions is changed.

Some Applications of Catalysis. Only a few of the many applications of catalysis in the realm of industrial chemistry can be mentioned here.

The Haber Process for Ammonia. By a careful study of the conditions governing the equilibrium represented by the equation,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

and by the employment of proper catalytic agents, Haber succeeded in producing ammonia on a commercial scale by means of this reaction. The synthesis of ammonia is now one of the large chemical industries of the world and is the basis of most of the world's explosives and much of its nitrogen fertilizer.

Pure iron and special alloys of iron are effective catalysts. A practical catalyst must be not only efficient but also stable and not too easily poisoned by traces of impurities.

In accordance with the principle of Le Chatelier, the equilibrium is shifted in the direction of the smaller volume, that is, in the direction of the ammonia, by an increase in pressure.

In order to obtain high yields of ammonia, the pressure is kept as high as is technically feasible, and the temperature is kept as low as possible. At 550° under a pressure of 200 atm nearly 12 per cent of ammonia is formed. The ammonia is removed and the remaining hydrogen and nitrogen is recirculated through the catalyst chamber.

Hydrogenation. Nickel catalysts and metallic oxide catalysts are used extensively for hydrogenating various liquids and dissolved substances with hydrogen under pressure. An important industrial ap-

plication of the hydrogenation process is the conversion of unsaturated aliphatic acids, such as oleic acid, into saturated acids, such as stearic acid.

By substituting various groups into a molecule it is possible to add hydrogen to different parts of a molecule. In the same way by adding certain hydrogen acceptors, that is, substances which are capable of taking up hydrogen, it is possible to remove hydrogen from different parts of a molecule with the help of a catalyst.*

Synthesis of Methanol. One of the outstanding developments in industrial chemistry has been the large-scale production of methyl alcohol from carbon monoxide and hydrogen using a zinc oxide–chromium oxide mixture as a catalyst.† The reaction is easily controlled, and the catalyst is not easily poisoned. Pressures up to 200 atm and temperatures between 200 and 400° are ordinarily used. Some of the higher alcohols have been synthesized in a similar manner, but it becomes increasingly difficult to suppress side reactions with the more complex molecules.

Petroleum Products. The most striking recent developments in catalysis have been made in the field of petroleum chemistry. Large-scale plants are now producing from ordinary petroleum a wide variety of products including toluene, butadiene for artificial rubber and isooctane and other compounds with high antiknock properties. Moreover, through this catalytic cracking it has been possible to increase greatly the amount of gasoline obtainable from the petroleum.

One of the chief difficulties in these catalytic operations has been the removal of the large amounts of heat formed by the chemical reactions. Fluidized catalysts are now used on a large scale, the catalyst in fine particles being transported in the gas stream. Intimate contact between catalyst and gas is thus assured, and supporting structures and expensive heat-transfer equipment are greatly reduced. Some of these large catalytic cracking towers are over 100 ft in height.

Fischer-Tropsch Synthesis of Hydrocarbons. Liquid fuel can be made from coal, methane, cellulose, or other carbonaceous material. The process was used on a large scale in Germany and is considered to be of importance in the United States in view of increasing demands for fuel oil for heating, for automobiles, and for Diesel engines.

Gas of the composition $n\mathrm{CO} + 2n\mathrm{H}_2$ is converted at comparatively low pressures into long-chain paraffin hydrocarbons using catalysts of cobalt, or of iron or nickel, at about 200°. The catalysts can be made by

* Adkins, "The Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937.

† Fenske and Frolich, *Ind. Eng. Chem.*, **21**, 1052 (1929); Smith and Hirst, *ibid.*, **22**, 1037, 1040 (1930).

coprecipitating cobalt and iron hydroxides on a silicious material and reducing to the metals. According to the carbide hypothesis, the carbon monoxide forms a carbide with the catalyst, and the carbon then combines with hydrogen which is loosely held by an adjacent part of the catalyst surface. Hydrocarbons of the form C_nH_{2n+2} are thus formed and removed in the gas stream and condensed. The carbon monoxide and hydrogen mixture called "synthesis gas" can be made from the partial combustion of methane, by the action of steam on coke, or by heating carbonaceous material. A large supply of cheap oxygen is needed because the use of air leaves an excess of nitrogen which then prevents proper operation of the process.

Decomposition of Hydrogen Peroxide. Many catalytic reactions are effected through a catalytic pair which is alternately oxidized and reduced. An example is the bromine–bromide catalysis of the hydrogen peroxide decomposition.* In acid solutions bromide ion is oxidized to hypobromous acid by hydrogen peroxide according to the equation,

$$H_2O_2 + Br^- + H^+ = HBrO + H_2O$$

and the hypobromous acid, in turn, is reduced by hydrogen peroxide according to the equation:

$$H_2O_2 + HBrO = H_2O + Br^- + H^+ + O_2$$

The second reaction is faster than the first, but eventually a *steady state* is reached in which the concentrations of bromide ion, hypobromous acid, and hydrogen ion are constant, and the only apparent change is

$$2H_2O_2 = 2H_2O + O_2$$

Enzymes. Many chemical reactions in living organisms are catalyzed by complex organic substances called enzymes produced by the living cell. They are complicated proteins having molecular weights of more than 50,000 and many of them have been isolated in apparently crystalline form. When isolated, they can carry on the same specific reactions in the laboratory (in vitro) as well as in the living organism (in vivo). *Catalase* exists in plant juice and in blood. It brings about the rapid decomposition of hydrogen peroxide. Dextrose is fermented to give ethanol and carbon dioxide by the enzyme *zymase* which is present in yeast. The enzyme *urease* catalyzes the hydrolysis of urea, to give ammonium bicarbonate and ammonium hydroxide.

Chain Reactions. The chain theory was first proposed by Bodenstein and by Nernst to account for the large yield obtained in the photo-

* Bray and Livingston, *J. Am. Chem. Soc.*, **45**, 1251 (1923).

chemical combination of chlorine and hydrogen to give hydrochloric acid. The reaction appears to be as follows:

$$Cl_2 + \text{light} = 2Cl$$

$$Cl + H_2 = HCl + H$$

$$H + Cl_2 = HCl + Cl$$

$$Cl + H_2 = HCl + H, \text{ etc.}$$

This cycle continues in some cases until over a million molecules have reacted. The chains can be started by other means than light, for example, by bombardment with alpha particles from radium, or by reaction with traces of sodium vapor, or by a spark.

One may ask why such a reaction ever stops. At times, as a matter of fact, the chain reaction does not stop until the material is consumed. At other times, however, the chain is broken when one of the activated molecules in the chain collides with the wall of the containing vessel or with foreign material which may be present as an impurity.

Certain oxidations in the gas phase have been explained successfully on the basis of chain reactions.* The specific velocity of the reaction depends among other things on the size of the vessel, the pressure of the gases, and the temperature because these factors affect the frequency with which the chain-propagating molecules hit the wall.

It is often difficult to distinguish a chain reaction from an ordinary reaction. Sometimes the presence of a chain mechanism can be established by determining that the number of molecules reacting is much larger than the number of molecules which are activated by the addition of a measured quantity of energy in a photochemical reaction. Again the presence of a chain may sometimes be revealed by the addition of retarding material called an inhibitor. Nitric oxide is an inhibitor for certain reactions in the gas phase.

If each molecule of the inhibitor stops a chain and each chain contains a great many molecules, it is obvious that mere traces of inhibitors are sufficient. For example, the oxidation of sodium sulfite by atmospheric oxygen is inhibited markedly by the addition of traces of alcohols. Lead tetraethyl in gasoline is another example of an inhibitor. Under certain conditions the chain reactions become too violent in a combustion engine, and a "carbon knock" is produced. A trace of the lead compound is sufficient to stop the chains and prevent the knock.

Still another example of the use of inhibitors is found in the preservation of gasoline. Certain unsaturated compounds in the gasoline tend

* Semenoff, *Chem. Rev.*, **6**, 347 (1929).

to polymerize and form gums in the presence of air and light. Indophenol, α-naphthol and certain other oxidizable substances containing phenolic and aromatic amine groups are effective in inhibiting this reaction. Antioxidants are becoming important also in preserving foods.

Free Radical Chains. In the decomposition of organic substances at high temperatures free radicals such as CH_3, C_2H_5, OH, H, and Br are formed, and they may propagate chain reactions. There is adequate evidence in band spectra for the existence of these free radicals which violate the rules of classical valence theories. Again their presence is revealed by the chemical removal of thin metallic mirrors. They are short-lived not because they are unstable but because they are extremely reactive. With these free radicals it is possible to set up a series of chain reactions in such a way that the over-all reaction is first order or second order or fractional order; and it is possible that they may play an important part in the mechanism of several reactions.

For example, the thermal decomposition of a hydrocarbon, such as propane, may involve the initial breakdown into free radicals, thus:

$$(1) \qquad C_3H_8 \rightarrow CH_3 + C_2H_5$$

$$(2) \quad CH_3 + C_3H_8 \rightarrow CH_4 + C_3H_7$$

$$(3) \qquad C_3H_7 \rightarrow CH_3 + C_2H_4$$

The CH_3 then continues as before:

$$(2') \quad CH_3 + C_3H_8 \rightarrow CH_4 + C_3H_7, \text{ etc.}$$

and the chain is propagated through a great many cycles until it is ended by a collision on the wall or by a combination of free radicals:

$$(4) \quad CH_3 + C_3H_7 \rightarrow C_4H_{10}$$

Other reactions go on also, but these will illustrate the possibilities and explain how methane, ethylene, and butane can be obtained from the decomposition of propane.

REFERENCES

Hinshelwood, "Kinetics of Chemical Change," Oxford University Press, Oxford, 1940.

Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, 1940.

Schumacher, "Chemische Gas Reaktionen," Steinkopf, Leipzig, 1938.

Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton University Press, Princeton, 1942.

Steacie, "Free Radicals," Rheinhold Publishing Corp., New York, 1945.

Daniels, "Chemical Kinetics," Cornell University Press, Ithaca, 1938.
Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932.
Symposia, *Chem. Rev.*, **10**, 1–264 (1932); **17**, 1–125 (1935); *J. Chem. Phys.*, **7**, 633–794 (1939).

PROBLEMS

1. The following data were obtained for the inversion of cane sugar where α_t is the reading of the polarimeter at time t:

t_{min}	0	10	20	40	80	180	300	∞
α_t	6.60	6.17	5.79	5.00	3.71	1.40	−0.24	−1.98

The reading α_∞ corresponds to the completion of the reaction, and $\alpha_t - \alpha_\infty$ is a measure of the sucrose remaining at any time. The α_∞ has a negative sign because the products, fructose and glucose, rotate polarized light in the opposite direction. Calculate k in reciprocal seconds (*a*) by formula; (*b*) by plotting $\log(\alpha_t - \alpha_\infty)$ against t.

Ans. 8.6×10^{-5} second^{-1}.

2. In a certain first-order reaction, half of the material is decomposed in 1000 seconds. (*a*) How long will it be until only one-tenth is left? (*b*) How many seconds are required for the reaction to be 99 per cent completed?

Ans. (*a*) 3322 seconds. (*b*) 6643 seconds.

3. A certain substance A is mixed with equal quantities of substances B and C. At the end of 1000 seconds half of A has reacted. How much will be left unreacted at the end of 2000 seconds if the reaction with respect to A is (*a*) first order; (*b*) second order in which equal parts of A and B react; (*c*) third order in which equal parts of A, B and C react; (*d*) zero order?

Ans. (*a*) 0.25. (*b*) 0.33. (*c*) 0.38. (*d*) 0.0.

4. The following specific reaction rates were obtained by Wiig for the first-order decomposition of acetone dicarboxylic acid in aqueous solution:

$t°$	0	20	40	60
$k \times 10^5$	2.46	47.5	576	5480

(*a*) Plot $\log k$ against $1/T$, and determine the energy of activation.
(*b*) Evaluate the constant s in the equation, $k = se^{-\Delta H_a/RT}$.
(*c*) What is the period of half-life of this reaction at 100°?

Ans. (*a*) 23,200. (*b*) 9.1×10^{13}. (*c*) 0.30 second.

5. Hydrogen is contained in a vessel at 1 mm pressure and 25°. Calculate (*a*) the number of collisions on the walls per second per square centimeter; (*b*) the number of collisions between molecules per second per cubic centimeter; (*c*) the mean free path.

Ans. (*a*) 1.44×10^{21}. (*b*) 2.52×10^{23}. (*c*) 0.0114 cm.

6. If a unimolecular reaction has an activation energy of 25,000 cal per mole and in the equation, $k = se^{-\Delta H_a/RT}$, s has a value of 5×10^{13}, at what temperature will the reaction have a half-life of (*a*) 1 minute; (*b*) 1 month of 30 days?

Ans. (*a*) 76°. (*b*) −4°.

---

7. From the following data on the rate of the rearrangement of 1-cyclohexenyl allylmalonitrile at 135.7°, determine graphically the first-order reaction-rate constant in reciprocal minutes. Check the graphical evaluation by calculating k from two different times.

Time (minutes)	0	5	10	20	30	45
Per cent rearranged	19.8	34.2	46.7	64.7	77.0	86.3

8. Prove that in a first-order reaction, where $dn/dt = -kn$, the average life, that is, the average life expectancy of the molecules, is equal to $1/k$.

9. The reaction, $CH_3CH_2NO_2 + OH^- \rightarrow H_2O + CH_3CH = NO_2^-$ is of second order, and k at 0° is 39.1 (mole/liter)$^{-1}$ minute^{-1}. An aqueous solution is made 0.004 molar in nitroethane and 0.005 molar in NaOH. How long will it take for 90 per cent of the nitroethane to react?

10. A second-order reaction where $a = b$ is 20 per cent completed in 500 seconds. How long will it take for the reaction to go to 50 per cent completion?

11. Show that the formulas,

$$k = \frac{2.303}{t_2 - t_1} \log \frac{c_1}{c_2}$$

$$k = \frac{2.303}{t_3 - t_2} \log \frac{c_2}{c_3} \quad \text{and} \quad k = \frac{2.303}{t_4 - t_3} \log \frac{c_3}{c_4}, \text{ etc.}$$

cannot be used for getting an average value of k by adding up k's from successive pairs of data and dividing by the number of k's taken.

12. Calculate the number of days required for 10 per cent of a mass of gaseous nitrogen pentoxide to decompose at −10° C.

13. The trichloroacetate ion in hydrogen-containing ionizing solvents decomposes into carbon dioxide and chloroform according to the reaction:

$$H^+ + CCl_3COO^- \rightarrow CO_2 + CHCl_3$$

The unimolecular breaking of the carbon–carbon bond in the trichloroacetate ion is probably the rate-determining step. The reaction is first order, and the specific rate constants are $k_{90°} = 3.11 \times 10^{-4}$, $k_{80°} = 7.62 \times 10^{-5}$, and $k_{70°} = 1.71 \times 10^{-5}$ second^{-1}. (*a*) Calculate the activation energy and (*b*) the specific rate constant at 60°. The experimentally determined value of k at 60° is 3.48×10^{-6}.

14. Calculate (*a*) the mean free path and (*b*) the number of collisions against the wall when 1 g of iodine is placed in a previously evacuated 2-liter spherical flask and heated to 100°.

15. The reaction,

$$Ge(C_2H_5)_4\,(g) \rightarrow Ge\,(s) + 4C_2H_5$$

has been studied by Geddes and Mack. The reaction is nearly independent of wall effects. The ethyl radicals combine to give a mixture of hydrocarbons with a higher pressure than the original germanium tetraethyl which they replace. The rate of the reaction can be calculated approximately from the rate of the pressure increase.

(*a*) Calculate k from the following data at 440.9°.

Time (seconds) $\times 10^{-1}$	0	23.1	38.4	56.6	75.9	93.6	∞
Total pressure (mm)	307	378	456	546	626	686	1079

(*b*) Calculate the activation energy and the frequency factor from the data of (*a*) and the additional data that $k = 0.00050$ at 431.1° and $k = 0.00024$ at 419.1°.

16. The velocity constant k for the third-order reaction expressed in moles per liter per second for the reaction,

$$2NO + O_2 \rightarrow 2NO_2$$

at 600° K is 6.63×10^5; at 645° K it is 6.52×10^5. For the reverse second-order reaction, k is 83.9 and 407 at these two temperatures.

(*a*) Calculate the equilibrium constants at the two temperatures.

(*b*) Calculate $\Delta E_{act.}$ for the forward and the reverse reactions.
(*c*) Calculate ΔE for the reaction, that is, the heat of reaction at constant volume.

---

17. A stream of air at 10 liters per minute, measured at 25° and 1 atm pressure, is passing through a catalyst tube which is 4 cm in diameter and 100 cm long, maintained throughout at 800°. Half the volume of the chamber is occupied by solid material. Approximately how many seconds does a given molecule remain in the catalyst chamber, if it is assumed that the gas reaches the temperature of the chamber 800° instantly?

18. In the saponification of ethyl acetate by sodium hydroxide at 10°, y ml of 0.056 molar hydrochloric acid was required to neutralize 100 ml of the reaction mixture, t minutes after the commencement of the reaction.

t	0	4.89	10.37	28.18	∞
y	47.65	38.92	32.62	22.58	11.48

Calculate the specific reaction-rate constant k, expressing the concentration in moles per liter and t in seconds.

19. The specific reaction rate k for the reaction,

$$2NO + O_2 \rightarrow 2NO_2$$

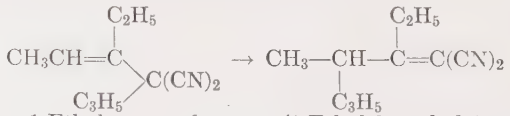
has a value of 7.1×10^9 mole^{-2} ml^2 second^{-1} at 25°. Air blown through a certain hot chamber and cooled quickly to 25° and 760 mm contains 1 per cent by volume of nitric oxide and 20 per cent of oxygen. (*a*) How long will it take for 90 per cent of this nitric oxide NO to be converted into nitrogen dioxide NO_2 (or N_2O_4)? (*b*) If the gases are blown through at the rate of 5000 cu ft per minute, how large a chamber must be constructed in order to obtain this 90 per cent conversion?

20. Referring to Fig. 94 in which $A \xrightarrow{k_1} B \underset{k_3}{\overset{k_2}{\leftrightarrows}} C$, prove mathematically that, regardless of the value of k_1, C_B and C_C will have the values 1/3 and 2/3 when the reaction is completed if k_2 is twice as large as k_3.

21. The reaction $2NO + O_2 \rightarrow 2NO_2$ follows the third-order law. Assuming that a small amount of N_2O_2 exists in rapid reversible equilibrium with 2NO, and that the rate-governing step is the slow bimolecular reaction $N_2O_2 + O_2 \rightarrow 2NO_2$, show that the reaction will nevertheless appear to be third order.

22. The decomposition of ethyl bromide is a first-order reaction with an activation energy of 54,800 cal. Estimate the temperature at which (*a*) ethyl bromide decomposes at the rate of $\frac{1}{10}$ of 1 per cent per second and (*b*) the decomposition is 90 per cent complete in 1 hour. $s = 3.8 \times 10^{14}$.

23. The rate of the rearrangement of 1-ethyl propenyl allyl malonitrile can be followed by measuring the refractive index. The reaction is



1-Ethyl propenyl allylmalonitrile → (1-Ethyl-2-methyl-4-pentenylidene)-malonitrile

The following first-order constants were obtained:

Temperature	120.0°	130.0°	140.0°
$k \times 10^4$	4.02	9.12	19.83

(*a*) What is the energy of activation?

(*b*) What is the frequency factor at 130.0°?

(*c*) What is the entropy of activation at 130.0°?

(*d*) Would you expect these three quantities calculated in (*a*), (*b*), and (*c*) to be practically the same at 120° and 140°?

24. In the reaction,

$$N_2 + O_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2NO$$

$$\frac{dx}{dt} = k_1\left(b - \frac{x}{2}\right)\left(c - \frac{x}{2}\right) - k_2x^2$$

where b is the original concentration of N_2, c is the original concentration of O_2, and x is the concentration of NO formed.

Values of the equilibrium constant K are given in Table V on page 281, where the concentrations are expressed in partial pressures in atmosphere. An estimate has been made of k_2 based on the Hirschfelder rule and on some experimental data according to which

$$k_2 = 1 \times 10^9\, e^{-70{,}000/RT} \text{ atm}^{-1} \text{ second}^{-1}$$

(*a*) Calculate k_1 at 2400° K and 1900° K.

(*b*) Calculate the time required for nitric oxide at 0.02 atm to undergo 10 per cent decomposition at 2400° K and at 1900° K, using k_2 and neglecting k_1.

25. Which of these two reactions is the more likely with chlorine atoms, (*a*) giving a free radical or (*b*) giving a hydrogen atom.

(*a*)
$$\begin{matrix} & R & \\ RC & — & H \\ & R & \end{matrix} + Cl = \begin{matrix} & R & \\ RC & & \\ & R & \end{matrix} + HCl$$

(*b*)
$$\begin{matrix} & R & \\ RC & — & H \\ & R & \end{matrix} + Cl = \begin{matrix} & R & \\ RCCl & & \\ & R & \end{matrix} + H$$

From a knowledge of the energies of dissociation or formation of the C–H, H–Cl and C–Cl bonds one can estimate the heat of reaction. As a rough approximation the entropy change may be disregarded and the sign and magnitude of the heat of reaction taken approximately as an indication of the free-energy change in the reactions. Those reactions which are highly endothermic will probably have a positive value of ΔF and will not be possible from a thermodynamic standpoint. They can then be ruled out in favor of a reaction which is highly exothermic and, therefore, likely to have a negative value of ΔF.

26. The thermal decomposition of gaseous acetaldehyde is a second-order reaction. The value of ΔH_a is 45,500 cal per mole, and the molecular diameter of the acetaldehyde molecule is 5×10^{-8} cm. (*a*) Calculate the number of molecules reacting per milliliter per second at 800° K and 760 mm pressure, and compare with the observed value 7.3×10^{16}. (*b*) Calculate k in moles per liter per second ($k = -1/c^2\, dc/dt$).

27. The energy of activation for the reaction, $C_2H_5Br \rightarrow C_2H_4 + HBr$, is 55,000 cal per mole. From this fact and Table III on page 134 show that the primary step in the dissociation cannot be the splitting off of a hydrogen atom nor a CH_3 group but that it can involve the splitting off of an HBr molecule, or (considering the inaccuracy of the data) that it can involve the splitting off of a bromine atom.

28. Solve the following differential equation for k:

$$\frac{dx}{dt} = k(a - x)(b - x)(c - x)$$

29. Given the consecutive unimolecular reactions:

$$A \xrightarrow[k=0.15]{} B \xrightarrow[k=0.1]{} C$$

plot curves which give the concentrations of A, B, and C as a function of time.

30. Carry out the integrations, and calculate the concentrations of A, B, and C shown in Fig. 94 for the three first-order reactions given by $A \xrightarrow{k_1} B \underset{k_3}{\overset{k_2}{\rightleftarrows}} C$.

31. Oxygen containing a few per cent of ozone is heated slowly from room temperature to 2500°. Explain any changes in the concentration of ozone which you would expect to find.

32. The recombination of free radicals requires very little activation energy. Give arguments then for the suggestion that the activation energy for an endothermic breaking of bonds to give radicals, such as a reaction $C_2H_5Br \rightarrow C_2H_5 + Br$, is about equal to the endothermic heat required to break the bonds.

33. A 3-liter container is filled with air at atmospheric pressure. In order to replace the air with carbon dioxide, the carbon dioxide is allowed to enter one end of the container at a rate of 2 liters a minute, and gas is allowed to escape from the other end at the same rate. If instant mixing of the gases is assumed, when will the partial pressure of oxygen be reduced to 0.01 mm?

34. In Problem 24 the recombination of nitrogen and oxygen was neglected. If the 0.02 per cent nitric oxide is mixed with 0.8 per cent nitrogen and 0.18 per cent oxygen, as it is if the nitric oxide is produced in air, the recombination should not be neglected. Using the notation of Problem 24 show that

$$k_2 \int_0^t dt = \int_0^x \frac{dx}{-x^2\left(1 - \frac{K^2}{4}\right) - \frac{K^2}{2}(b + c) + K^2bc}$$

Integrate this expression, and suggest how simplifying assumptions may render more practical the calculations of the concentrations of nitric oxide at various time intervals.

35. Propellants of nitrocellulose burn very rapidly inward from the surface—at a rate of the order of 1 linear cm per second at atmospheric pressure. There are roughly 10^8 nitrogen atoms per linear centimeter. Parts of the molecule probably break off at the surface and combine in the gas phase giving a flaming envelope around the surface which raises the surface to a high temperature. The higher the pressure, the faster is the reaction and the higher is the temperature.

Assuming that the primary reaction at the surface is a unimolecular bond-breaking process at 1000° with an activation energy of 46,000 cal per mole of N, calculate the specific reaction rate k defined by the expression,

$$\frac{dn}{dt} = kn$$

where dn/dt is the number of molecules decomposing per second and n is the number of molecules at the surface which are potentially decomposable. Show how this expression can then be used to estimate the linear rate of burning.

CHAPTER XV

ELECTRIC CONDUCTANCE

Historical Introduction. Although early observations pointed to the probability of the existence of some relation between chemical and electrical phenomena, it was not until the beginning of the nineteenth century that the discovery by Volta of a means of obtaining electric energy from chemical energy gave the initial impulse to all the investigations on which modern electrochemistry is based. Volta prepared a series of zinc and silver disks, arranged them alternately with paper soaked in salt water between them, and thus made a source of electricity available for experimentation.

In 1800 Nicholson and Carlisle decomposed water by electrolysis, and Davy isolated alkali metals by means of an electric current. From his experiments Davy formulated an electrochemical theory, but this was soon superseded by the theories of Berzelius that every atom has both negative and positive charges, that the behavior of the atom is determined by the kind of electricity which is in excess, and that chemical attraction is between oppositely charged atoms. Berzelius' theories were, in turn, superseded. It was difficult to explain how negative chlorine atoms combine with each other to give chlorine molecules or how two positive hydrogen atoms combine to form hydrogen. It remained for recent theories of atomic structure to offer an explanation.

The importance of electric charges in inorganic compounds and in solutions of electrolytes has been fully recognized since physical chemistry became a separate branch of chemistry in the late 1880's. The important part played by electric interaction among neutral molecules in organic chemistry has been realized however only during the past quarter century. The dipole moment, the concept of the electronic pair, the electron theory of valence and the explanation of electrolysis and oxidation and reduction through the transfer of electrons are all comparatively recent developments which have contributed much to the advancement of science. The quantitative relations between electricity and chemical change are discussed in the three chapters which follow.

Electrical Units. According to Ohm's law discovered in 1827,

$$I = \frac{E}{R} \tag{1}$$

where I is the current in amperes, E is the difference in voltage applied or the voltage, and R is the resistance in ohms.

The *international ohm* is defined as the electrical resistance equal to that of a column of pure mercury at 0° 106.300 cm in length and of such constant cross section that the column contains 14.4521 g of mercury.

The *international ampere* is defined as that current which under specified standard conditions will deposit 0.001118 g of silver per second from a solution of silver nitrate.

The *coulomb* of electricity is that quantity of electricity which passes a given cross section of a conductor in 1 second while a current of 1 ampere is flowing.

The *volt* is the potential difference which causes a current of 1 ampere to flow through a conductor which has a resistance of 1 international ohm.

Electric energy is the product of an intensity factor, voltage, and a quantity factor, coulombs, as pointed out on page 100. Thus

$$\text{Electric energy in joules} = \text{volts} \times \text{coulombs}$$

Electric energy may also be divided into a power factor, the *watt*, or *volt-ampere*, and a time factor, the second. One watt-second is 1 volt × 1 ampere × 1 second, or 1 joule. One kilowatt-hour is equal to 3,600,000 joules. The "defined calorie" is now defined in physical chemistry as 4.1840 absolute joules.*

In addition to these practical units there are the electrostatic units, esu, and the electromagnetic units, emu. If two equal charges 1 cm apart in a vacuum repel each other with a force of 1 dyne, each charge is equivalent to 1 electrostatic unit. The electromagnetic unit of current is a current such that when it flows through a conductor 1 cm long bent in an arc of 1 cm radius, the force on a unit magnetic pole at the center of the circle will be 1 dyne.

Starting January 1, 1948, the U. S. Bureau of Standards recommended, in accordance with international agreement, the absolute units which differ slightly from the international values that had been used heretofore. New precision instruments will be calibrated in terms of the

* Formerly it was defined as 4.1833 international joules which is equal to 4.1840 absolute joules.

newly adopted values and will be marked "abs." The changes are too small to consider in most practical laboratory work.*

Electric Conductance. There are two different types of electric conductance: metallic conduction as, for example, in a copper wire, and electrolytic conductance as, for example, in a solution of salt in water. In metallic conduction the electricity appears to be a stream of electrons flowing toward the positive terminal. In electrolytic conductance electricity is carried in solution by ions. Positive ions move toward the negative electrode, and negative ions move toward the positive electrode, and both share in carrying the current. In metallic conduction there is no change in the chemical properties of the conductor, but in electrolytic conductance, chemical reactions are produced at the electrodes, and matter is transported to the electrodes.

Both types of electric conductance involve the generation of more or less heat, depending on the electric resistance of the system. As a general rule the metallic conductors become less conducting at high temperatures, whereas the electrolytic conductors become more conducting. In the former case, the electrons find it more difficult to pass through the crystal lattice when the units of the lattice are in thermal agitation; and, in the latter case, the ions can move through the solution more readily, because the viscosity is less, and the solvation of the ions is less. In some cases the number of ion carriers is changed by an increase in temperature.

Electricity may be carried by electrons across an evacuated space as in an ordinary electron or radio tube. The electrons are emitted by a heated wire and drawn to a positively charged plate. Electricity may be carried also by means of gas ions, as in an electrical discharge. The gas ions are charged positively or negatively, and they move in a manner somewhat analogous to the movement of electrolytic ions. There are several points of difference, however. The gas ions may have several different charges, and there is little connection between the valence and the charge, whereas in electrolytic ions the charge is closely connected

* The new values given in circular of the National Bureau of Standards C 459 are as follows:

International Standards	Absolute Values
1 ohm	1.000495 absolute ohm
1 volt	1.000330 absolute volt
1 ampere	0.999835 absolute ampere
1 coulomb	0.999835 absolute coulomb
1 joule	1.000165 absolute joule

Formerly the international joule was considered as equal to 1.00020 absolute joules.

with the valence. The electrolytic ions are present before the electrodes are charged, the large energy required for ionization being supplied from the solvation of the ions. Most of the gas ions, however, are produced only after the electrodes are charged, the energy required for ionization being supplied by collisions of charged particles in the electric field. It is necessary to have a few gas ions to start with, but these are always present as a result of cosmic rays and traces of radioactive materials.

Electrical resistance is directly proportional to the length of the conductor and inversely proportional to its cross section. The specific electrical resistance (the resistance of a cube 1 cm on an edge) of various materials is given for the sake of comparison in Table I.

TABLE I

Electrical Resistance of Typical Conductors

Material	Temperature	Specific Resistance, ohm-cm
Silver	0°	1.468×10^{-6}
Copper	0°	1.561×10^{-6}
Aluminum	0°	2.564×10^{-6}
Iron	0°	9.070×10^{-6}
Lead	0°	20.480×10^{-6}
Mercury	0°	95.85×10^{-6}
Fused $NaNO_3$	500°	0.568
Fused $ZnCl_2$	500°	11.93
1 *M* KCl	25°	8.93
0.001 *M* KCl	25°	6,810
1 *M* acetic acid	18°	757.5
0.001 *M* acetic acid	18°	24,400
Water	18°	2.5×10^{7}
Xylene	25°	7×10^{18}

In the neighborhood of absolute zero the resistance of metals becomes extremely low. The specific resistance of mercury at 3° K, for example, is less than 10^{-8} ohm.

Measurement of Conductance of Solutions. In the Wheatstone bridge shown in **Fig. 100,** *C* is the cell containing the solution whose resistance is to be measured, and *R* is a resistance box. The resistance coil at *ab* is adjusted by rotating contacts so as to change the ratio *ad*/*bd* by multiples of ten. The resistance *R* is changed by turning dials which make contact with a varying number of coils of resistance wires.

Alternating current of about a thousand cycles, which gives a high mosquito-like noise in the telephone T is generated at A. A better type of cell for precision measurements is shown in the lower right-hand corner. Cells with long paths are better for concentrated solutions, and those with short paths are better for dilute solutions.

Alternating current is necessary to prevent complications at the electrodes. Direct current produces gas bubbles on the electrodes which greatly increase the resistance, and the current changes the concentration of electrolytes in the neighborhood of the electrodes. If the alternating current is not of a pure sine-wave type with positive and negative potentials exactly offsetting each other, it is necessary to platinize the electrodes. This coating adsorbs the gases and catalyzes their reaction. The current may be generated with an electrically driven tuning fork or, better, with an oscillating circuit composed of radio tubes with proper capacities and inductances.

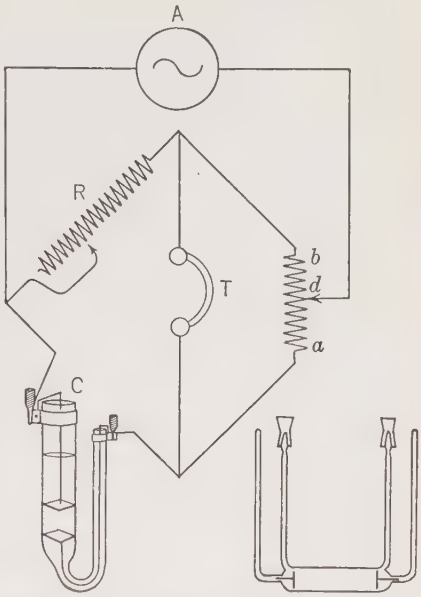


FIG. 100. Wheatstone bridge and cell for determining the electric conductance of solutions.

In making a measurement of the unknown resistance C, the known resistance R and the resistance ratio ad and bd are adjusted until the sound in the telephone is barely audible, that is, the sound is at a minimum. Then the two terminals of the telephone are at the same potential, and the potential drop $\boldsymbol{E}$ across the different parts of the bridge must be such that $\boldsymbol{E}_C = \boldsymbol{E}_R$ and $\boldsymbol{E}_{ad} = \boldsymbol{E}_{bd}$. Moreover, since the drop in potential $\boldsymbol{E}$ is equal to the current I multiplied by the resistance

$$I_C C = I_R R \quad \text{and} \quad I_{ad} ad = I_{bd} bd$$

Dividing the first equation by the second gives

$$\frac{I_C C}{I_{ad} ad} = \frac{I_R R}{I_{bd} bd} \tag{2}$$

Furthermore, $I_R = I_{bd}$ and $I_C = I_{ad}$, since the current flowing through the two resistances in series must be the same in each resistance when

no current flows through the telephone. Then canceling out these equalities in equation 2, we have

$$\frac{C}{ad} = \frac{R}{bd}$$

or

$$\frac{C}{R} = \frac{ad}{bd} \tag{3}$$

This is the fundamental formula for the use of the Wheatstone bridge. In modern bridges the ratio ad/bd is arranged to give only 0.01, 0.1, 1, 10, 100, etc., so that no numerical calculations are necessary.

Specific and Equivalent Conductance. The *specific resistance* of an electrolyte may be defined as the resistance in ohms of a column of solution 1 cm long and 1 sq cm in cross section. The *specific conductance* L is the reciprocal of the specific resistance. It is expressed in reciprocal ohms, sometimes called *mhos*. The units of specific conductance are $\text{ohm}^{-1}\ \text{cm}^{-1}$.

The *equivalent conductance* Λ is obtained by multiplying the specific conductance L by the volume V in milliliters* which contains 1 gram equivalent of solute, that is, by $1000/c$ where c is the number of gram equivalents per liter.

$$\Lambda = VL = \frac{1000L}{c}\ \text{cm}^3\ \text{equiv}^{-1}\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

$$= \frac{1000L}{c} = \text{cm}^2\ \text{equiv}^{-1}\ \text{ohm}^{-1}\ * \tag{4}$$

These relations may be illustrated by imagining a cell 1 cm square and indefinitely high. Two opposite walls are of conducting metal which act as electrodes. When the cell is filled to a height of 1 cm, the conductance measured is the specific conductance. When the cell is filled with a given volume V of solution which contains 1 gram equivalent of a dissolved electrolyte, the solution will stand V centimeters high in the cell, and the conductance measured under these conditions will be the equivalent conductance.

The term *molar conductance* is defined as in equation 4 except that the concentration is given in moles per liter instead of gram equivalents per liter.

In determining specific resistance it would be troublesome to prepare a cell having electrodes exactly 1 cm^2 in area and exactly 1 cm apart.

* There is a slight inaccuracy here involving the small difference between ml and cm^3. In electric-conductance measurements, the cubic centimeter is often used in preference to the milliliter.

However, it is not necessary to do this, because it is possible to determine a factor, called the cell constant. The cell constant of any cell is determined experimentally with a standard solution of known specific conductance. Measurements on any other solution may then be converted directly into specific conductances. A 0.0200-molar solution of potassium chloride is generally used for the determination of the cell constant. It has the following specific conductances:

$$L_{18°} = 0.002394 \quad \text{and} \quad L_{25°} = 0.002768 \text{ ohm}^{-1} \text{ cm}^{-1} *$$

If r is the resistance of the cell, when filled with 0.0200 molar potassium chloride, $1/r$ is the conductance, and the specific conductance L is equal to $k(1/r)$, where k is the proportionality constant or cell constant, which converts conductance, as measured in a given cell, into specific conductance.

Then

$$k = Lr \tag{5}$$

When a cell is filled with 0.0200-molar potassium chloride at 25°,

$$k = 0.002768r$$

When the cell constant k has been determined, the specific conductance of any solution is obtained from the measured resistance r by the relation,

$$L = \frac{k}{r} \tag{6}$$

Example 1. When a certain conductance cell was filled with 0.02 M KCl, it had a resistance of 82.4 ohms at 25° as measured with a Wheatstone bridge; and, when filled with 0.0050 N K_2SO_4, it had a resistance of 326 ohms.

(*a*) What is the cell constant?

$$k = 0.002768 \times 82.4 = 0.2281$$

(*b*) What is the specific conductance L of the potassium sulfate solution?

$$L = \frac{k}{r} = \frac{0.2281}{326} = 0.0006997$$

(*c*) What is the equivalent conductance?

$$\Lambda = 0.0006997 \times \frac{1000}{c} = \frac{0.6997}{0.0050} = 139.9 \text{ cm}^2 \text{ equiv}^{-1} \text{ ohm}^{-1}$$

* The data of Jones and Bradshaw, *J. Am. Chem. Soc.*, **55**, 1780 (1933) are now taken as the standard for exact work in electrolytic conductance. When 0.745263 g of pure potassium chloride is weighed out into pure water to give 1000 g of solution (corrected to vacuum), the specific conductances are as follows: 0°, 0.0007736; 18°, 0.0012205; 25°, 0.0014087 ohm^{-1}. This solution contains 0.01 mole per cubic decimeter (which differs very slightly from a liter).

Conductance of Different Electrolytes. Table II gives the specific and equivalent conductances of aqueous solutions of potassium chloride at 25°.

TABLE II

CONDUCTANCE OF POTASSIUM CHLORIDE AT 25°

Equivalents per liter c	Dilution, ml per Equivalent, V	Specific Conductance, L	Equivalent Conductance, Λ
1	1,000	0.1119	111.9
0.1	10,000	0.01289	128.9
0.01	100,000	0.001413	141.3
0.001	10^6	0.0001469	146.9
0.0001	10^7	0.00001489	148.9

It may be observed that, when the volume is increased tenfold and the number of equivalents per milliliter is decreased to one tenth, the specific conductance decreases nearly but not quite to one-tenth its value. The equivalent conductance, on the other hand, changes only slightly but does increase and approach a limiting value at greater dilutions.

In very dilute solutions of potassium chloride there is no appreciable change in equivalent conductance when the solution is diluted with an equal volume of water. Although the volume is doubled and the number of ions per milliliter is halved, the *total* number of ion carriers between the tall electrodes is still the same. In more concentrated solutions of potassium chloride, however, the equivalent conductance increases on dilution, because the ions move faster when they are farther apart and are not held back by the ions of opposite charge which they tend to drag along.

In solutions of acetic acid the situation is quite different, and the equivalent conductance increases markedly on dilution, because the solute dissociates more at the greater dilution giving a considerable increase in the total number of ions, that is, the number of the carriers of electricity.

Electrolytes may be divided into two general classes: the *strong electrolytes*, such as potassium chloride, with high conductances and slight increases on dilution; and *weak electrolytes*, such as acetic acid, with low conductances and larger increases in conductance on dilution. In general, the strong electrolytes include many inorganic acids such as hydrochloric and sulfuric acid, most salts, and the alkaline hydroxides. The

weak electrolytes, on the other hand, include the carboxylic acids and many organic acids and bases. There are of course a great many electrolytes which fall between these two extremes and have properties intermediate between strong electrolytes and weak electrolytes.

Table III gives the equivalent conductances of several typical electrolytes, from normal down to so-called "zero" concentration. For these

TABLE III

Equivalent Conductances of Electrolytes at 25°

Equivalents per liter (N)	NaCl	KCl	HCl	NaOH	$AgNO_3$	$CaCl_2$	$LaCl_3$	$NaC_2H_3O_2$	$HC_2H_3O_2$[1]
0.0000	126.5	149.9	426.1	248	133.4	135.8	145.9	91.0	(390.7)
0.0005	124.5	147.8	422.7	246	131.4	131.9	139.6	89.2	67.7
0.001	123.7	146.9	421.4	245	130.5	130.4	137.0	88.5	49.2
0.005	120.6	143.5	415.8	240	127.2	124.2	127.5	85.7	22.9
0.01	118.5	141.3	412.0	237	124.8	120.4	121.8	83.8	16.3
0.02	115.8	138.3	407.2	233	121.4	115.6	115.3	81.2	11.6
0.05	111.1	133.4	399.1	227	115.2	108.5	106.2	76.9	7.4
0.10	106.7	129.0	391.3	221	109.1	102.5	99.1	72.8	5.2

[1] Acetic acid is a weak electrolyte, and the conductance at infinite dilution is obtained by indirect methods. All the other electrolytes given in the table are strong electrolytes.

electrolytes it may be observed that the equivalent conductance increases with the dilution of the solution until a limiting value Λ_0 is reached. It is important to bear in mind that, although Λ_0 is frequently referred to as the conductance at infinite dilution, it is by no means identical with the conductance of the pure solvent. In fact it is necessary in accurate work, particularly at low concentrations, to subtract the conductance of the solvent from that of the solution in order to obtain the conductance due to the electrolyte. Thus,

$$L_{\text{solute}} = L_{\text{solution}} - L_{\text{solvent}} \tag{7}$$

The purest water has a specific resistance of about 20 million ohms, but it is difficult to obtain water with much over a million ohms specific resistance because of the absorption of carbon dioxide and other gases from the atmosphere and of alkali and other electrolytes from the glass-containing vessel. Ordinary distilled water in equilibrium with air has a specific resistance of only about 100,000 ohms.

Conductance data are shown graphically in **Fig. 101,** where it may be noted that the equivalent conductance of the strong electrolytes such as

hydrochloric acid reaches a limiting value at the higher dilutions. The weak electrolytes, such as acetic acid, however, do not reach such a limiting value within regions which can be studied experimentally. Below concentrations of 0.0001 molar the conductance of the solvent itself becomes relatively large, and traces of carbon dioxide or ammonia from the air, or alkali from the glass, introduce large errors.

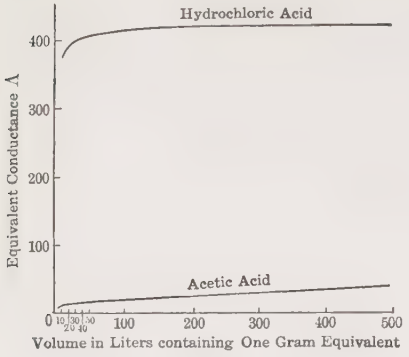


FIG. 101. Equivalent conductance of a weak electrolyte, acetic acid, and a strong electrolyte, hydrochloric acid, at different dilutions.

When the equivalent conductance of strong electrolytes is plotted against the square root of the concentration, the line is nearly straight at the low concentrations as shown in **Fig. 102.** Extrapolation of this line to infinite dilution gives an accurate value of Λ_0. A weak electrolyte, on the other hand, gives steep curves which can be extrapolated to infinite dilution only with great difficulties and inaccuracies. Values at

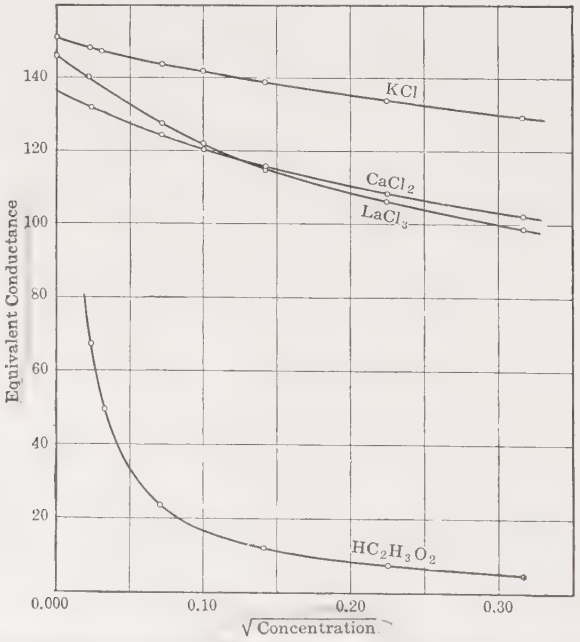


FIG. 102. Equivalent conductance of typical electrolytes plotted against the square root of the concentrations.

infinite dilution must be determined indirectly, as shown on page 416. This equivalent conductance at infinite dilution is important in calculating the degree of dissociation of a weak electrolyte, as indicated on page 484.

The equivalent conductance of electrolytes increases with temperature owing to the increased mobility. Typical of this temperature effect are the conductances of potassium chloride and silver nitrate shown in Table IV.

TABLE IV

Equivalent Conductances in Water at Different Temperatures

Solute	Concentration	0°	18°	100°	140°	156°	218°	306°
KCl	0.08*N*	72.3	113.5	341.5	455	...	...	720
KCl	0.002*N*	79.6	126.3	393	534	...	...	1008
$AgNO_3$	0.08*N*	....	96.5	294	...	432	552	604

Electrolysis. Thus far we have considered some of the factors involved in the conductance of solutions due to the movement of electrically charged ions when two charged electrodes are placed in a solution of the ions. Before proceeding further, we must examine the changes which take place at the electrodes while the ions are carrying the current.

The two conducting pieces of metal, which serve as electrodes, dip into the solution of electrolyte and are charged negatively and positively by being connected to a dynamo or an electric battery. Units of electricity, the negative electrons, are drawn by the dynamo from one electrode and fed into the other. If a battery is used, the chemical reactions of the battery remove electrons from one electrode and supply them to the other electrode. The electrode to which the extra electrons are fed becomes negatively charged and attracts the positive ions. This negative electrode through which negative electrons are fed into the electrolytic solution is called the cathode, and the positive ions which migrate to it and remove the electrons are called cations. The other electrode is positively charged, and it attracts the negative ions and removes their electrons. It is called the anode, and the ions which move toward it are called anions. At the anode a stream of electrons is discharged from the negative ions in the solution to the electrode and, thence, into the electric circuit.

The removal or addition of electrons is a matter of the utmost importance, not only in electrolysis but also in many chemical reactions.

The removal of electrons is oxidation. It occurs at the anode.

The addition of electrons is reduction. It occurs at the cathode.

Thus, in electrolysis, ferric ions are reduced to ferrous ions at the cathode:

$$Fe^{+++} + e = Fe^{++}$$

and ferrous ions are oxidized to ferric ions at the anode:

$$Fe^{++} = Fe^{+++} + e$$

Usually there are several different kinds of ions around each electrode competing for electrons at the cathode and competing for an opportunity to give up electrons at the anode. Furthermore, it is quite likely that one or more secondary reactions will follow the primary electrode reaction in which there is a transfer of an electron. Some chemical experience is necessary in order to predict what will happen. For example, if chlorine is liberated in an alkaline solution, hypochlorite or chlorate may be formed. If chlorine is liberated on a silver anode, silver chloride is formed.

If a copper anode is used in the electrolysis of a solution of cupric chloride, the copper will simply go into solution and take the place of the copper which goes out of solution at the cathode. If a platinum anode is used, the platinum cannot go into solution, and oxygen is liberated from the water. When several different ions are competing for the transfer of an electron, several possibilities occur, depending on the concentration and on the energies involved. If there are no easily reducible cations around the cathode, hydrogen will be produced from the hydrogen ions of water leaving an excess of hydroxyl ions, and, if there are no easily oxidizable anions around the anode, the hydroxyl ions will be removed with the formation of oxygen. Under certain conditions these reactions lead to an alkaline reaction at the cathode and an acid reaction at the anode, thus explaining the common litmus paper test used to determine whether a given electrode is positive or negative. Litmus turns blue at the cathode due to the alkaline reaction and it turns red at the anode.

In Table V are listed several reactions which are typical of the mechanisms by which changes take place during electrolysis. The electron is designated by e.

These changes occur when direct current is passed in the same direction from one electrode to the other through the cell. When the direction of the current is reversed rapidly, that is, 60 times per second, the products

given by these reactions do not have a chance to accumulate before they are removed again. In experiments dealing with the conductance of the solution, alternating current is generally used in order to eliminate chemical reactions at the electrodes which change the resistance of the cell as a whole. In experiments dealing with electrolysis at the electrodes it is obviously necessary to use direct current.

TABLE V

Typical Electrolysis Reactions

Electrolyte	Electrodes	Cathode Reaction	Anode Reaction
H_2O	Platinum	$H^+ + e = \frac{1}{2}H_2$	$OH^- - e = \frac{1}{4}O_2 + \frac{1}{2}H_2O$
$AgNO_3$	Silver	$Ag^+ + e = Ag$	$Ag - e = Ag^+$
$AgNO_3$	Platinum	$Ag^+ + e = Ag$	$OH^- - e = \frac{1}{4}O_2 + \frac{1}{2}H_2O$
$Fe_2(SO_4)_3$	Platinum	$Fe^{+++} + e = Fe^{++}$	$OH^- - e = \frac{1}{4}O_2 + \frac{1}{2}H_2O$
$FeSO_4$	Platinum	$H^+ + e = \frac{1}{2}H_2$	$Fe^{++} - e = Fe^{+++}$
NaI	Platinum	$H^+ + e = \frac{1}{2}H_2$	$I^- - e = \frac{1}{2}I_2$
NaI	Silver	$H^+ + e = \frac{1}{2}H_2$	$I^- - e = AgI$
$PbCl_2$	Platinum	$Pb^{++} + 2e = Pb$	$Cl^- - e = \frac{1}{2}Cl_2$; $OH^- - e = \frac{1}{4}O_2 + \frac{1}{2}H_2O$

Faraday's Law. Faraday studied these phenomena of electrolysis with clear insight and announced in 1834 that for the same electrolyte the weight of material reacting in electrolysis is proportional to the quantity of electricity flowing; and that for a given quantity of electricity the weights of different substances liberated are proportional to the weights of their chemical equivalents.

Faraday's law may now be stated as follows:

In electrolysis, 96,500 coulombs of electricity produce a chemical change of 1 gram-equivalent. For example, 96,500 coulombs (or ampere-seconds) will liberate 1.0080 g of hydrogen, and it will deposit from solution 107.88 g of silver, 63.54/2 g of copper from cupric salts, and 197.2/3 g of gold from auric solutions. The name *faraday* and the symbol F are given to this important quantity of electricity.

This law is one of the most exact laws in physical chemistry; it has been found to hold at low and high temperatures, in dilute and concentrated solutions, at various pressures and in different solvents. When the law does not appear to hold, it can usually be shown that secondary chemical reactions are obscuring the primary electron-transferring reaction at the electrode to which the law is intended to apply.

Faraday's law can be clearly understood with the help of the hypothesis that atoms are composed of positive nuclei surrounded by negative electrons. When an electron is removed from an atom, the remaining ion is positively charged. When an extra electron becomes attached to an atom, a negative ion is produced. If the ions are bivalent, two electrons are involved.

When cupric chloride is dissolved in water, each of the two chloride ions holds an extra electron obtained originally from a copper atom which then becomes a divalent positive ion. Every time two electrons are supplied to the cathode, they become attached to one of the cupric ions which happens to be in contact with the cathode; an atom of copper is formed by the addition of two electrons to the cupric ion, which then deposits on the electrode. For every electron supplied to the cathode, one electron is withdrawn from the anode, and so it is obvious that the same amount of electrochemical action must occur at each electrode. At the anode the electrons are taken from the chloride ions in contact with the anode.

Electrolysis involves, then, a transfer of electrons between the electrodes and the surrounding ions, and Faraday's law is simply the result of counting off one electron for each univalent atom, or two electrons for each divalent ion, etc. Each gram atom of a univalent element contains 6.0235×10^{23} atoms, and, accordingly, it will take 6.0235×10^{23} electrons to deposit 1 gram atom in electrolysis. The charge on the electron is 1.6020×10^{-19} coulomb (Chapter XXI), and so the coulombs required to electrolyze a gram atom of a univalent ion are

$$6.0235 \times 10^{23} \times 1.6020 \times 10^{-19} = 96{,}496 \qquad (8)$$

This number is in agreement with the value already given. As a matter of fact, the experimental determination of the value of the faraday and the charge on the electron provide one of our best means for determining the value for the Avogadro number, 6.0235×10^{23}.

Since Faraday's law involves only a counting process, it is evident why the law is so exact. Its accuracy is limited only by the accuracy of measuring the chemical change and the quantity of electricity.

Not only does Faraday's law provide a means for calculating the amount of electrochemical reaction during electrolysis, but it provides also a means for determining the quantity of electricity which has passed through a circuit from a measurement of the amount of electrochemical reaction. Even though the current may fluctuate over wide ranges, the total quantity of electricity in coulombs or ampere-seconds which has passed can be determined chemically in a coulometer. The silver coulometer, in which silver is deposited from a solution of silver nitrate and

weighed on a platinum cathode, is perhaps the most accurate. Usually a weighed platinum dish holds the solution and serves as the cathode. Other types of coulometers depend on the weight of copper deposited, the amount of oxygen and hydrogen liberated, the volume of mercury produced from a mercury salt, or the quantity of iodine liberated at the anode and titrated.

Example 2. A current of 0.100 ampere is passed through a copper sulfate solution for 10 minutes using platinum electrodes.

(*a*) Calculate the number of grams of copper deposited at the cathode.

$$\frac{10 \times 60 \times 0.100}{96{,}500} \times \frac{63.54}{2} = 0.01975 \text{ g}$$

(*b*) Calculate the number of atoms deposited.

$$\frac{10 \times 60 \times 0.100}{96{,}500} \times \frac{1}{2} \times 6.02 \times 10^{23} = 0.1872 \times 10^{21}$$

(*c*) Calculate the volume of oxygen liberated at the anode at 25° and 740 mm.

$$\frac{10 \times 60 \times 0.100}{96{,}500} \times \frac{\frac{16}{2}}{32} \times \frac{82.05 \times 298.1}{\frac{740}{760}} = 3.92 \text{ ml}$$

Migration of Ions. The current is carried through the wire by electrons, but it is carried through the solution by positive ions moving toward the cathode and by negative ions moving toward the anode. It is not necessary that the two ions carry the same fractions of the current even though they may have the same valence. The fraction of the current carried through the solution is a function of the relative velocities with which the cation and the anion move. The ions which move faster carry the larger quantity of electricity through the solution in a given time, that is, they carry the larger fraction of the current. If v_c is the velocity of the cation and v_a is the velocity of the anion, then the transference number n_c of the cation is the fraction of the current carried by the cation as given by the following equation:

$$n_c = \frac{\text{current carried by cation}}{\text{total current}} = \frac{v_c}{v_c + v_a} \qquad (9)$$

Likewise, the transference number of the anion n_a is equal to $v_a/(v_c + v_a)$. It is obvious that

$$n_c + n_a = 1$$

These fractions, n_a and n_c, called the *transference numbers*, were first investigated by Hittorf in 1853.

During electrolysis the concentration around the two electrodes is changed both by the chemical changes taking place at the electrodes and by the migration of cations and anions. The way in which these changes are effected is illustrated diagrammatically in **Fig. 103.** The solution undergoing electrolysis is divided into three compartments with

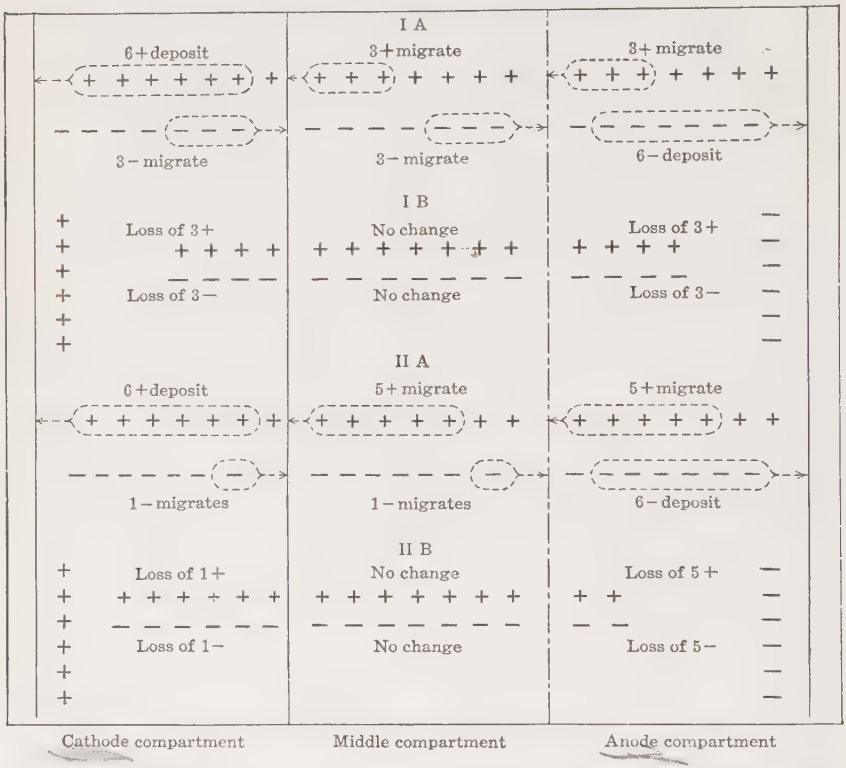


FIG. 103. Schematic representation of change in concentrations produced in the neighborhood of electrodes by passage of electric current.

imaginary partitions. The concentration is uniform throughout the vessel before the electrolysis, and it is assumed for the sake of discussion that there are seven positive and seven negative ions in each compartment and that the current is passed long enough to deposit six ions. Six electrons are removed from the anode and supplied to the cathode, and accordingly six cations are discharged at the cathode, and six anions are discharged at the anode.

In the first case shown in Fig. 103 it is assumed that the cations and anions have the same velocity and each carries half the current. Accordingly, three positive charges are carried between the electrodes by

the cations, and three negative charges are carried in the opposite direction by the anions. The movement of the ions is indicated by dotted lines in IA and the net result is shown in IB. Six cations have been deposited at the cathode, three have moved into the cathode compartment from the middle compartment, and three have moved into the middle compartment from the anode compartment. Similar changes have occurred with the anions. The net result of migration and electrolysis is to decrease the concentration in the neighborhood of the electrodes from seven to four and to leave the concentration unchanged in the middle compartment.

When the transference numbers of the two ions are not equal, the change in concentration is different at the two electrodes, as shown at IIA and IIB. In hydrochloric acid, for example, the hydrogen ion travels about five times as fast as the chloride ion, and, at room temperature, $n_c = 0.83$ and $n_a = 0.17$. Six ions are discharged at each electrode as before, but in this case five sixths of the current is carried by the hydrogen ion and one sixth by the chloride ion. The changes are indicated by dotted lines and arrows in IIA, and the net result is shown in IIB. Six hydrogen ions are discharged at the cathode, but five move in from the middle compartment, giving a net loss of one hydrogen ion. There is also a loss of one chloride ion due to migration. Six chloride ions are discharged at the anode, but only one migrates into the anode compartment, and the net loss around the anode is five. There is also a loss of five hydrogen ions, owing to migration toward the cathode.

Transference Numbers by Change in Concentration. If the cation moves faster than the anion, it will carry a larger fraction of the current, and it will tend to increase in concentration around the cathode. Designating a gram equivalent by ϵ the change in concentration at the cathode which is due to migration, $\Delta\epsilon_{\text{migration}}$, divided by the total number ν of faradays of electricity, passed through the cell is a measure of the fraction of the current carried by the cation. Thus, for the cation,

$$n_c = \frac{\Delta\epsilon_{\text{migration of cation}}}{\nu F} \qquad (10)$$

and, in a similar way for the anion,

$$n_a = \frac{\Delta\epsilon_{\text{migration of anion}}}{\nu F}$$

where ν, the total number of faradays is equal to the sum of the number of equivalents of cation and anion migrating. The concentration of the electrolyte in the neighborhood of an electrode depends not only on the migration of the ions but also on the electrochemical changes

taking place at the electrode. Thus the total change $\epsilon_{\text{final}} - \epsilon_{\text{initial}}$ or $\Delta\epsilon$ is given by the expression,

$$\Delta\epsilon = \Delta\epsilon_{\text{migration}} + \Delta\epsilon_{\text{electrolysis}}$$

or

$$\Delta\epsilon_{\text{migration}} = \Delta\epsilon - \Delta\epsilon_{\text{electrolysis}} \tag{11}$$

$\Delta\epsilon$, which may have either a positive or a negative value, is determined by analyzing the solution around the electrode before and after electrolysis.

The quantity νF is calculated from coulometer determinations or, less accurately, from measurements of amperes and seconds. The quantity $\Delta\epsilon_{\text{electrolysis}}$ is calculated from νF and a knowledge of the chemical reaction taking place at the electrode. If the ion is deposited at the electrode, its concentration will decrease, and $\Delta\epsilon_{\text{electrolysis}}$ has a negative value. $\Delta\epsilon_{\text{migration}}$ is then calculated by equation 11 and n_c or n_a is calculated by equation 10. In calculating transference numbers the number of gram equivalents per gram of water is multiplied by the number of grams of water taken in the sample. The sample must be large enough to include all the solution in the neighborhood of the electrode. Usually the electrode is placed in a compartment from which the solution can be drained and analyzed. The quantity $\Delta\epsilon$ is determined by subtracting the number of equivalents contained in a given weight of water from the number of equivalents originally present before electrolysis in exactly the *same weight* of water. A determination of the equivalents per volume of solution does not give accurate results, because the concentration and, hence, the density of the solution changes during the electrolysis.

Example 3. An aqueous solution of copper sulfate was electrolyzed between copper electrodes. On the cathode 0.3000 g of copper was deposited. The solution in the anode compartment contained 1.4300 g of copper after electrolysis, and the same weight of water originally contained 1.2140 g before electrolysis. Calculate the transference numbers of the ions.

$$\Delta\epsilon = \epsilon_{\text{final}} - \epsilon_{\text{initial}}$$

For the Cu^{++} with an equivalent weight of 63.54/2 or 31.77,

$$\Delta\epsilon = \frac{1.430}{31.77} - \frac{1.2140}{31.77} = \frac{0.216}{31.77}$$

= total increase of copper in the anode compartment

$$\Delta\epsilon_{\text{electrolysis}} = \frac{0.300}{31.77}$$

= increase of copper in the anode compartment coming from anode

and

$$\nu F = \frac{0.300}{31.77} = \text{equivalent of electricity passed through the cell}$$

Then,

$$\Delta\epsilon_{\text{migration}} = \Delta\epsilon - \Delta\epsilon_{\text{electrolysis}} = \frac{0.216}{31.77} - \frac{0.300}{31.77} = -\frac{0.084}{31.77}$$

There has been a change of 0.084/31.77 equivalents due to migration. The negative sign of $\Delta\epsilon_{\text{migration}}$ indicates that copper ions have migrated out of the anode compartment,

$$n_{Cu^{++}} = \frac{\Delta\epsilon_{\text{migration}}}{\nu F} = \frac{\frac{0.084}{31.77}}{\frac{0.300}{31.77}} = 0.28$$

and

$$n_{SO_4^{--}} = 1 - 0.28 = 0.72$$

Table VI gives the transference numbers of the cations of several typical electrolytes, at different concentrations. The transference num-

TABLE VI

TRANSFERENCE NUMBERS OF CATIONS AT 25°

Electrolyte	0.01 N [1]	0.05 N	0.1 N	Electrolyte	0.01 N [1]	0.05 N	0.1 N
HCl	0.825	0.829	0.831	$AgNO_3$	0.465	0.466	0.468
$NaC_2H_3O_2$	0.554	0.557	0.559	$LaCl_3$	0.462	0.448	0.437
KNO_3	0.508	0.509	0.510	$K_3Fe(CN)_6$	0.431	0.439	0.441
NH_4Cl	0.491	0.491	0.491	$CaCl_2$	0.426	0.414	0.406
KCl	0.490	0.490	0.490	NaCl	0.392	0.388	0.385
KBr	0.483	0.483	0.483	LiCl	0.329	0.321	0.317

[1] Equivalents per liter.

bers of the corresponding anions can be found by subtracting the transference numbers of the cations from unity.

The transference numbers vary slightly with the concentration. They depend on the relative ionic diameters and particularly on the extent to which the ions are solvated. Those ions which are extensively solvated, such as calcium and lithium, move slowly on account of the extra solvent molecules which they must drag along, and, accordingly, they have small transference numbers.

The fact that ions are hydrated may be shown by an experiment on transference numbers in which sugar is added to the solution.* The sugar is not moved by the potential gradient, but, when the solution around the electrodes is examined with a polarimeter, the concentration

* Washburn and Millard, *J. Am. Chem. Soc.*, **37**, 694 (1915).

of sugar becomes less in the compartment into which the hydrated ions migrate. The solution becomes diluted by the water dragged along with the ions.

Hydrogen ions and hydroxyl ions possess abnormally high velocities in water, possibly because the proton can be transferred from molecule to molecule.

Ionic Mobilities. The absolute velocity of ions may be determined directly by measuring the distance traveled in a given period of time under a definite potential gradient. A solution of one electrolyte is carefully floated on top of another in a long vertical tube of uniform diameter. A line of demarkation between a colored and a colorless solution provides the simplest means of observation, but uncolored ions may be traced by the absorption of ultraviolet light or by the distortion of a scale viewed through the boundary between the two liquids where there is an abrupt change in refractive index. In order to keep the boundary sharp the two ions are chosen so that the slower ion follows the faster ion. Mechanical stirring is avoided by selecting electrodes which will give no evolution of gas.

The velocities of ions are summarized in Table VII where the mobilities are given in centimeters per second at 25° under a potential gradient of 1 volt per centimeter.

TABLE VII

Ionic Mobilities at 25°

Ion	Mobility	Ion	Mobility	Ion	Mobility	Ion	Mobility
H^+	0.00362	Cl^-	0.00079	Ba^{++}	0.00066	HCO_3^-	0.00046
OH^-	0.00205	K^+	0.00076	$Cr_2O_7^{--}$	0.00054	Li^+	0.00040
SO_4^{--}	0.00083	NO_3^-	0.00074	Na^+	0.00052	Cu^{++}	0.00036

It may be noted that, aside from the hydrogen and hydroxyl ions, most of the ions have velocities of the order of 3 to 8×10^{-4} cm per second or about 2 cm per hour at 25° under a potential gradient of 1 volt per centimeter.

Transference Numbers by Moving Boundary.* Transference numbers may be determined in a manner similar to that just described for

* MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939, Chapter 4.

measuring ionic mobilities. As shown in **Fig. 104,** two solutions with different colors or different refractive indices are placed in a tube which is graduated in fractions of milliliters. When a difference in potential is applied to the electrodes, the movement of the boundary B is observed, and the volume swept out by the moving ion is recorded.* In Fig. 104 the upper electrode is of silver–silver chloride and the lower electrode is of cadmium. The tube is filled with hydrochloric acid and an indicator. When the circuit is closed, the fast hydrogen ions move upward, followed by the slower cadmium ions produced at the anode, and the acid color of the indicator marks sharply the boundary between the two. The current of about 0.010 ampere is kept constant by regulating the adjustable rheostat.

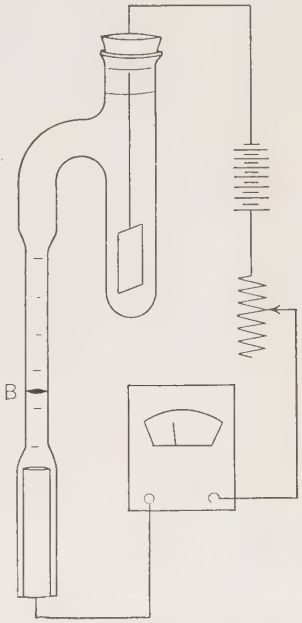


FIG. 104. Apparatus for determining transference numbers by a moving boundary.

If c equivalents of the electrolyte (hydrochloric acid in this case) is dissolved in a liter of solution, the volume in milliliters containing 1 gram equivalent is $1000/c$. When 1 faraday $\boldsymbol{F}$ of electricity passes through the solution, there will be a movement of 1 equivalent of electrolyte, or $1000/c$ ml of solution. Of this volume of solution $n_c(1000/c)$ ml will be swept out by the cation and $n_a(1000/c)$ ml by the anion. If a smaller quantity of electricity f is passed, a smaller volume, v milliliters, will be swept out by the cation and measured in the graduated tube. Then,

$$\frac{f}{\boldsymbol{F}} = \frac{v}{n_c(1000/c)} \tag{12}$$

Since the current is kept constant, the number of coulombs f is equal to the time t in seconds multiplied by the current i in amperes. Then,

$$n_c = \frac{v\boldsymbol{F}c}{1000ti} \tag{13}$$

A similar formula may be derived for the anion.

* MacInnes and Longsworth, *J. Am. Chem. Soc.*, **60,** 3070 (1938); Longsworth, *J. Chem. Education,* **11,** 420 (1934).

Example 4. In a vertical moving boundary apparatus for transference numbers the cathode was placed at the top. The anode at the bottom was surrounded by lithium chloride; on top of this solution was sodium chloride solution, and on top of that was sodium acetate surrounding the cathode. The sodium ion moves faster than the lithium ion, and the chloride ion moves faster than the acetate ion. If the chloride–acetate boundary moved down 8.06 mm while the sodium–lithium boundary moved up 4.94 mm, calculate the transference numbers of chloride and sodium ions. Since the charge on each ion, the current, the time, the cross section of the tube, and the concentration were the same for the two ions,

$$n_a = \frac{8.06}{8.06 + 4.94} = 0.62 \quad \text{and} \quad n_c = \frac{4.94}{4.94 + 8.06} = 0.38$$

Ionic Conductances. As early as 1875 Kohlrausch examined the equivalent conductances of many different electrolytes and came to the conclusion that *at infinite dilution* the ions behave independently, so that the equivalent conductance of the electrolyte Λ_0 is equal to the sum of the equivalent conductances of the cations $l_{0,c}$ and anions $l_{0,a}$, thus:

$$\Lambda_0 = l_{0,c} + l_{0,a} \tag{14}$$

This law of Kohlrausch is supported, for example, by the fact that

$$\Lambda_{0,\,KCl} - \Lambda_{0,\,NaCl} = 149.9 - 126.5 = 23.4 \text{ cm}^2 \text{ equiv}^{-1} \text{ ohm}^{-1}$$

$$\Lambda_{0,\,KI} - \Lambda_{0,\,NaI} = 150.3 - 126.9 = 23.4 \text{ cm}^2 \text{ equiv}^{-1} \text{ ohm}^{-1}$$

This constant difference of about 23.4 is always found between a potassium and a sodium salt of the same acid at infinite dilution. It is easily explained on the basis that the conductance of the potassium ion is 23.4 more than that of the sodium ion, that the anion is the same in both cases, and that the conductance depends only on the presence of the independent ions.

Kohlrausch's law is useful in calculating the equivalent conductance at infinite dilution of the weak electrolytes which cannot be determined by direct extrapolation.

Example 5. Calculate the equivalent conductance of acetic acid at infinite dilution at 25°. Extrapolation gives the following values at infinite dilution,

$$\Lambda_{0,\,HCl} = 426.1; \qquad \Lambda_{0,\,NaC_2H_3O_2} = 91.0; \qquad \Lambda_{0,\,NaCl} = 126.5$$

$$(l_{0,\,H^+} + l_{0,\,Cl^-}) + (l_{0,\,Na^+} + l_{0,\,C_2H_3O_2^-}) - (l_{0,\,Na^+} + l_{0,\,Cl^-}) = l_{0,\,H^+} + l_{0,\,C_2H_3O_2^-}$$

$$\Lambda_{0,\,HCl} + \Lambda_{0,\,NaC_2H_3O_2} - \Lambda_{0,\,NaCl} = \Lambda_{0,\,HC_2H_3O_2}$$

$$\Lambda_{0,\,HC_2H_3O_2} = 426.1 + 91.0 - 126.5 = 390.6 \text{ cm}^2 \text{ equiv}^{-1} \text{ ohm}^{-1}$$

The method of differences illustrated in this problem gives the equivalent conductances of a weak electrolyte, but it does not permit a calculation of the individual ionic conductances. They may be calculated,

however, with the help of the transference numbers. The transference number is the fraction of the total current carried by the given ion, which, in turn, is the ratio of the conductance of the ion to the conductance of all the ions, that is, to the conductance of the electrolyte.

Thus,

$$n_c = \frac{l_c}{l_c + l_a} = \frac{l_c}{\Lambda} \tag{15}$$

and

$$l_c = n_c \times \Lambda \tag{16}$$

Also,

$$l_a = n_a \times \Lambda$$

With equations 14 and 16 it is possible to determine the equivalent conductances at infinite dilution of weak electrolytes.

Example 6. Calculate Λ_0 for acetic acid at 25° at infinite dilution, using the data of Tables III and VI.

$$l_{0,\,H^+} = n_{0,\,c} \times \Lambda_{0,\,HCl} = 0.82 * \times 426.1 = 349.4$$

$$l_{0,\,C_2H_3O_2^-} = n_{0,\,a} \times \Lambda_{0,\,NaC_2H_3O_2} = 0.45^* \times 91.0 = 40.9$$

$$\Lambda_{0,\,HC_2H_3O_2} = l_{0,\,H^+} + l_{0,\,C_2H_3O_2^-} = 390.3$$

When the conductance of one ion at infinite dilution is determined, others may be obtained from the equivalent conductances of the electrolytes by simple subtraction, using equation 14. An average of several chlorides gives Λ_{0,Cl^-} as 76.3 ohm^{-1}. Then, for example,

$$l_{0,\,K^+} = \Lambda_{0,\,KCl} - l_{0,\,Cl^-} = 149.9 - 76.3 = 73.6$$

In this way Table VIII has been constructed.

TABLE VIII

Ionic Conductances at Infinite Dilution at 25°

Cations	l_c	a	Anions	l_a	a
H^+	349.8	0.014	OH^-	198	0.016
K^+	73.5	0.019	$\frac{1}{3}Fe(CN)_6^{---}$	101.0	.....
NH_4^+	73.4	0.019	$\frac{1}{2}SO_4^{--}$	79.8	0.020
$\frac{1}{3}La^{+++}$	69.6	.....	Br^-	78.4	0.019
$\frac{1}{2}Ba^{++}$	63.6	0.020	I^-	76.8	0.019
Ag^+	61.9	0.020	Cl^-	76.3	0.019
$\frac{1}{2}Ca^{++}$	59.5	0.021	NO_3^-	71.4	0.018
$\frac{1}{2}Mg^{++}$	53.1	0.022	HCO_3^-	44.5	.....
Na^+	50.1	0.021	$C_2H_3O_2^-$	40.9	.....
Li^+	38.7	0.023			

* Extrapolated values.

With this table it is easy to calculate equivalent conductances of many different electrolytes at infinite dilution, or to calculate transference numbers.

The temperature coefficient is given under the columns a, where a is defined by the equation,

$$l_{0,\,t} = l_{0,\,25}[1 + a(t - 25)] \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

for the ionic conductance at temperatures t not far removed from 25°. It may be noted that most of these values give a change of about 2 per cent per degree which is about the same as the temperature coefficient of the viscosity of water. This relationship is explained by the theory that each ion moving through the solution carries with it an atmosphere of solvent, and the frictional resistance offered to the motion of the ion is the frictional resistance between masses of pure water.

As already explained, the ions which are most heavily hydrated have small transference numbers. According to this hypothesis, the most heavily hydrated ions lose more of the water of hydration when heated, and, accordingly, they have larger temperature coefficients of conductance. Furthermore, since the increase in temperature accelerates the velocity of the highly hydrated slow-moving ions more than it accelerates the fast-moving ions, there is a tendency to equalize the velocities and bring both transference numbers more closely to the limiting value of 0.5 at higher temperatures.

Conductance of Nonaqueous Solutions. Although the study of nonaqueous solutions has been quite limited in comparison with the extensive studies of aqueous solutions, there is much of theoretical significance and practical importance to be obtained from investigations of nonaqueous solutions.* In several respects water is an abnormal solvent, and a broader knowledge of electrical behavior in other solvents has led to important contributions to the theory of solutions.

Only those substances, such as salts, acids, and bases, which can dissociate into ions and only those solvents with reasonably large dielectric constants and dipole moments are of interest in conductance studies. Solvents such as benzene and carbon tetrachloride with very small dipole moments do not interact with the solutes sufficiently to pull the charged parts apart and produce ions. The viscosity of the solvent is a factor of lesser importance in studying the conductance of solutions. Among the solvents that have been important in the conductance of nonaqueous solutions are alcohols, liquid ammonia, dioxane, acetone

* Kraus, "The Properties of Electrically Conducting Systems," Chemical Catalog Co., New York (1922).

and other ketones, anhydrous formic acid and acetic acid, pyridine and several amines and nitro compounds.

A few miscellaneous examples of conductances in nonaqueous solutions are given in Table IX.

TABLE IX

Conductance of Nonaqueous Solutions

Solvent	Temperature, °C	Electrolyte	Concentration, Equivalents per liter	Specific Conductance	Equivalent Conductance
Ammonia	−33	NaI	1.14	0.28	245
Ethanol	18	NaI	1.00	0.035	35.2
Acetone	25	NaI	1.0		26.4
			0.1		64.1
			0.01		109.7
			0.0		(176.2)
Isoamyl alcohol	25	NaI	0.1		1.29
			0.01		2.02
			0.00		(7.79)
Methyl amine	−33	KI	9.3	0.17	17.7
Ethyl amine	−33	$AgNO_3$	8.0	0.0083	1.04
Nitromethane	25	KI	10.0	0.88	88.1
Ammonia	−33	Na	0.8	1.27	2017

The conductance of metallic sodium in liquid ammonia is interesting. Apparently, the neutral sodium atoms dissociate into positive Na^+ ions and negative electrons.

The conductance in mixtures of solvents can be predicted in some cases by assuming that the effects are additive. In other cases the conductance becomes quite complicated. For example, both pure water and pure sulfuric acid have extremely low conductances, but mixtures of the two are conducting. As the sulfuric acid concentration increases, the specific conductance increases until a maximum of about 0.72 is attained at about 33 per cent H_2SO_4 after which the conductance decreases until a minimum is reached at 85 per cent, corresponding to the compound $H_2SO_4 \cdot H_2O$. Further increase in concentration of H_2SO_4 causes an increase in conductance to a slight maximum and then a decrease to a very low value at 100 per cent H_2SO_4. Addition of SO_3 to the H_2SO_4 again gives an increase in conductance.

Crystalline salts have very low conductances because the ions are held in fixed positions, but the fused salts are excellent conductors. Even

in the crystal form the conductance becomes appreciable at temperatures just below the melting point, a fact which shows that there is some mobility of the ions. Impurities in the salt sometimes give an abnormally large conductance. The specific conductance of many fused salts is large, sometimes exceeding the conductance of the most concentrated aqueous solutions, but the equivalent conductance is comparatively small on account of the high concentration of the electrolyte. The electrolysis of fused salts finds important technical applications in such operations as the production of sodium from fused sodium hydroxide, the production of magnesium from fused magnesium chloride, and the production of aluminum on an enormous scale by the electrolysis of fused aluminum hydroxide dissolved in molten sodium aluminum fluoride. Electrolysis in fused salts and nonaqueous solutions makes possible the production of certain metals which cannot be deposited in the presence of water.

Table X lists a few examples of the conductance of fused salts.

TABLE X

Conductance of Fused Salts

Salt	Temperature, °C	Specific Conductance	Equivalent Conductance
AgCl	600	4.16	111
AgBr	600	3.08	51.9
AgI	600	2.43	64.6
$AgNO_3$	250	0.83	36.1
	350	1.25	55.4
$NaNO_3$	350	1.17	52.9
	450	1.56	73.1
KNO_3	350	0.67	26.5

Conductimetric Titrations. The electrical conductance of a solution serves as a means for determining the end point in chemical reactions, such as titrations of acids and bases, or precipitations.

For example, when a strong acid is added to a strong base, the conductance decreases to a minimum, at which the base is completely neutralized, and then it increases owing to the excess of acid, as shown in **Fig. 105** for sodium hydroxide and hydrochloric acid. The two lines AB and CD intersect at the point E which is the end point. The OH^- ions of the base and the H^+ ions of the acid have a much greater velocity

than the sodium and chloride ions, and so the conductance is least at the end point E where the acid and base are present in exactly equivalent portions, and there is no excess of either OH^- ions or H^+ ions. In order that the lines AB and BC shall be straight and thus permit calculations from sets of only two points, it is desirable to keep the volume constant throughout the titration. In order to approach this condition, the added reagent must be concentrated, whereas the solution which is being titrated must be dilute.

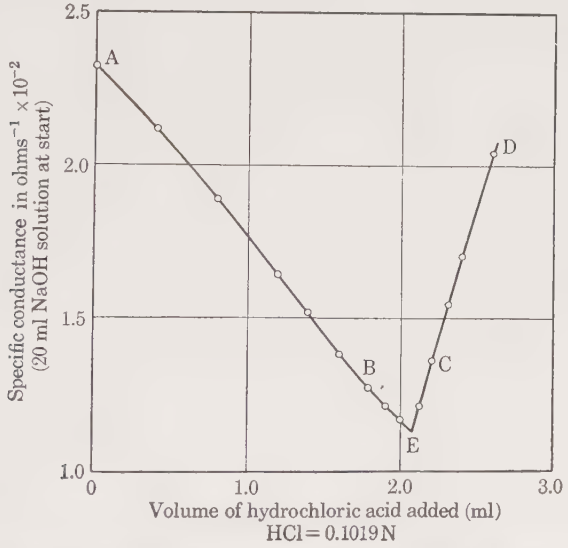


FIG. 105. Electric conductance in the titration of a strong base NaOH by a strong acid HCl.

If the same titration is carried out with a weak acid, acetic acid, instead of a strong acid, as shown in **Fig. 106,** the excess acid beyond the end point will not cause such a sharp increase in conductance. In fact, with acetic acid a horizontal line is obtained after all the sodium hydroxide has been neutralized, because the number of conducting ions being added in the excess of acetic acid is small, particularly in the presence of the sodium acetate (as explained on page 488). The sharp change in the slope of the line is useful, however, in determining end points. In colored or turbid solutions, where a colored indicator cannot be used, this determination of end points by means of conductance measurements is particularly useful. In practical work it is often convenient to plot resistance or merely bridge readings instead of specific conductances. Moreover, good end points can be obtained with resistance measurements of only moderate accuracy.

End points in precipitations can be determined by conductance measurements, because the ions left in solution will have somewhat different ionic conductances from the ions which are removed from solution in the precipitation. One of the best reactions for this method is the precipitation of a salt like magnesium sulfate with barium hydroxide, because

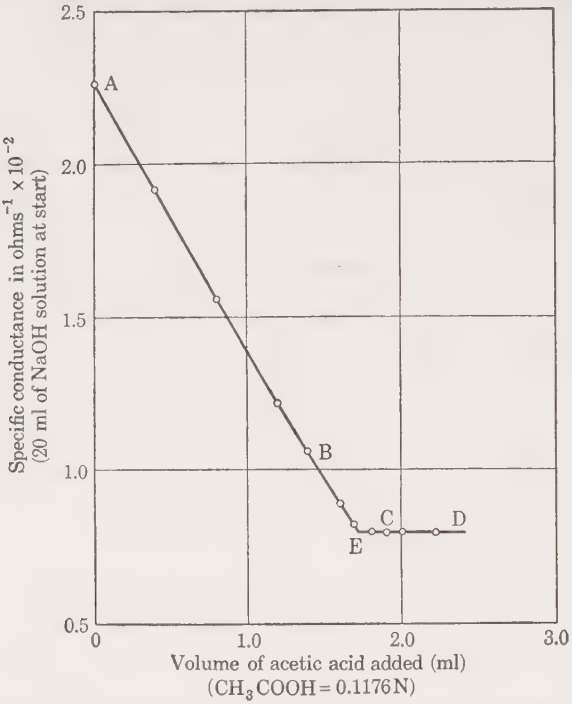


Fig. 106. Electric conductance in the titration of a strong base NaOH by a weak acid CH_3COOH.

in this case both products $BaSO_4$ and $Mg(OH)_2$ are insoluble, and the conductance at the end point is very low.

Conductance measurements are used for a variety of testing and control operations, such, for example, as concentration by evaporation of acids or salts, leakage of salt solutions, hardness of water, moisture content of soil or wood, and rates of chemical reaction in which the products have a different conductance from that of the reactants.

Decomposition Voltage. When two platinum electrodes are placed in a solution of an electrolyte and a low voltage is applied, practically no current flows through the circuit. As the voltage is gradually increased, there may be a temporary flow of current until the products accumulate and produce an opposing voltage and cause the current to

diminish. However, for each electrolyte there is voltage above which a large current continues to flow. This voltage is called the *decomposition voltage.* At voltages above the decomposition voltage the current is proportional to the applied voltage. When the current flowing is plotted against the applied voltage as shown in **Fig. 107,** the extrapolation of the steep line to cut the horizontal axis gives a measure of the decomposition

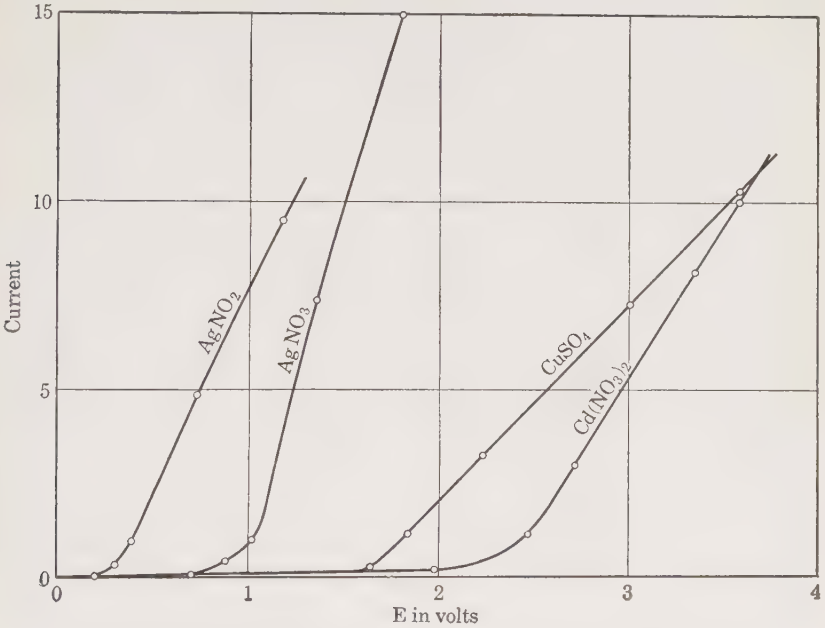


FIG. 107. Determination of decomposition potentials of salts.

voltage.* In another method the applied voltage is increased until bubbles of gas or deposits of metal on an electrode can be detected with a microscope. Decomposition voltages vary with the conditions, but are characteristic of definite electrolytes. Thus the decomposition voltage of copper sulfate is 1.6, of lead nitrate is 1.8, and of cadmium nitrate is 2.3 volts. It is a striking fact that most strong acids and bases have decomposition potentials of 1.7 volts. They all behave alike in that at 1.7 volts or above they give off hydrogen and oxygen at the electrodes. Acids such as concentrated hydrochloric acid, which give products other than hydrogen and oxygen, have decomposition potentials which are below 1.7 volts.

The decomposition potentials play a role in the controlled deposition of metals or other electrolytic products when a potential difference is ap-

* Groening and Cady, *J. Phys. Chem.*, **30,** 1597 (1926).

plied to the electrodes of an electrolytic cell containing several different electrolytes; the one with the lowest decomposition potential is electrolyzed first, and, as the voltage is increased, other salts are electrolyzed and other metals deposited in turn as their decomposition potentials are exceeded.

For example, in a mixture of cadmium, lead, and silver which is subjected to electrolysis, the decomposition potentials of the salts are as follows: $Cd(NO_3)_2$ = 2.3 volts, $Pb(NO_3)_2$ = 1.8 volts, and $AgNO_3$ = 0.9 volt. If the applied electromotive force is made a little less than 1 volt, the silver will be deposited; then, if the electromotive force is raised to about 1.9 volts, the lead will be deposited; and finally, if the electromotive force is raised above 2.3 volts, the cadmium will be deposited.

If a platinum anode is surrounded by a solution of chloride ions in water, both Cl^- ions and OH^- ions will be colliding with the electrode and competing for the removal of the electron. Less energy is required to discharge the hydroxyl ion. Therefore, when Cl^- and OH^- ions are in nearly the same concentration, practically pure oxygen will be evolved, but, when the chloride ion is in large excess, chlorine gas will be produced at the anode. In 2 *M* hydrochloric acid chlorine is evolved, but in 0.02 *M* solution oxygen is evolved, whereas at intermediate concentrations a mixture of chlorine and oxygen is obtained. Thus, it is seen that the products of electrolysis can be controlled not only by changing the applied voltage but also by changing the concentrations. When there are different kinds of ions competing at an electrode for the loss or gain of electrons, there are two factors involved—the decomposition potential which is a measure of the energy requirement and the concentration which is a measure of the frequency of collision with the electrode surface.

If a solution of potassium sulfate is electrolyzed, hydrogen and oxygen are evolved because the hydrogen and hydroxyl ions are discharged at a lower voltage than the potassium ions and sulfate ions, as indicated by the normal electrode potentials. However, with very large current densities it is possible to deplete the hydrogen ions in the immediate neighborhood of the cathode to such an extent that some potassium will then deposit in a mercury cathode.

The deposition of metals can be altered by changing the solvent. Thus hydrogen is deposited at the cathode in an aqueous solution of sodium iodide, but sodium is deposited from a solution of sodium iodide in dry acetone.

The control of concentration as well as voltage is important in practical electroplating. In nickel plating, for example, if the acidity of the plating baths exceeds a certain limit, hydrogen will be liberated, and the

deposit will not be firm and smooth. The electroplating of a mixture of copper and zinc (brass) is another example. Ordinarily, when a mixture of zinc and copper salts is electrolyzed, copper is plated exclusively, because its decomposition potential is much less. However, the concentration of copper ions can be decreased enormously by adding potassium cyanide and locking up most of the copper in complex ions; under these conditions, when the zinc is very concentrated, both metals will be deposited together at the cathode.

Important changes in the electrodeposition of metals can be made through the use of rapidly rotating electrodes. When the solution in the neighborhood of the electrode is removed rapidly, there is less chance for a change in concentration due to electrolysis. Smooth deposits can then be formed even with high current densities. If the solution is not agitated, the current must often be kept so low as to require long times for deposition. Sometimes the introduction of a colloid like gelatine into the solution produces smaller crystals and a smoother deposit on the electrode.

The Dropping-Mercury Electrode.* The decomposition voltages obtained with a dropping-mercury electrode cathode are now often used for chemical analysis of inorganic and organic substances. Heyrovsky first developed a sensitive apparatus called the polarograph, which automatically records the current as the voltage is gradually increased. Each reducible substance has a definite characteristic decomposition potential, and the voltage at which the current increases rapidly is used for qualitative analysis. Furthermore, the magnitude of the current flowing at the decomposition voltage enables one to make an empirical calculation of the concentration of the material present which is undergoing reduction. The electrode surface is being continuously renewed as the mercury flows down from a small capillary, and the current passing across the boundary of the electrode depends on the rate at which the material in contact with the cathode can be reduced. This rate is proportional to the concentration of the material in the solution film surrounding the cathode. The concentration depends on the rate at which the material diffuses to the fresh film of the cathode surface, and this, in turn, depends on the concentration in the body of the solution. There are other factors involved, but simple satisfactory analyses have been made on a great many different substances using empirical calibrations with known concentrations under conditions which are the same as those existing in the "unknown" solution.

* Kolthoff and Lingane, *Chem. Rev.*, **24**, 1 (1939); "Polarography," Interscience Publishers, New York, 1941; O. H. Müller, *J. Chem. Education*, **18**, 65, 111, 172, 227 (1941).

Polarization. The production of a countervoltage by the products of electrolysis is called *polarization*. For example, if a current of electricity is passed through a solution of lead chloride between platinum electrodes, lead will be deposited on the cathode and chlorine on the anode. The lead–chlorine cell thus formed causes current to flow in the opposite direction and opposes the impressed voltage. Polarization may be caused also merely by the change in concentration of the electrolytes around an electrode produced by the electrolysis, thus leading to the production of voltage, as explained on page 454. The polarization of an electrode can be determined by measuring the potential of the electrode against a reference electrode, such as a calomel electrode described on page 434, before and after the passage of the current. Polarization does not occur when all the reactions are rapid and the electrode is in a state of reversible equilibrium. The existence of polarization implies that one of the reaction steps involved is slow.

Overvoltage is a special case of polarization which depends on the evolution of gas. It is the difference between the decomposition voltage at which gas is evolved on an electrode and the voltage at which it is evolved under reversible conditions, as on a platinized platinum electrode. The overvoltage depends on the nature of the electrode, on the current density, and on other factors. The overvoltages for the liberation of hydrogen at a current density of 0.1 ampere per square centimeter are roughly as follows: platinized platinum 0.0; polished platinum 0.3; gold 0.6; iron 0.8; silver 0.9; nickel 1.02; zinc 1.1; lead 1.2; tin 1.2.

The decomposition potential must be at least as great as the equilibrium electrode potentials, given in the electromotive-force series on page 447, plus the overvoltages. The overvoltage of lead is responsible for a higher voltage for the storage battery, and the overvoltage of zinc is responsible for the moderate resistance of zinc to corrosion. Many electroplating operations also involve overvoltages.

Electrolytic Reduction and Oxidation. Electrolysis provides a simple and effective means for the reduction of inorganic and organic materials. Electrolytic reduction depends on the supply of electrons produced at the cathode. Either hydrogenation or electrolysis or both may take place, depending on the conditions. Likewise, oxidation may be produced electrolytically by removing electrons at the anode; and sometimes the oxygen liberated at the anode can be used to advantage. In some operations a porous cup is placed in the cell to keep the cathode and anode gases separated from each other. In some electrochemical reactions the hydrogen liberated at the cathode is an important factor.

The current density, the cathode potential, the acidity of the solu-

tion, the overvoltage, and the nature of the electrode surface affect the electrolytic hydrogenation and reduction at the cathode.

The conversion of nitrobenzene into aniline is one of the classic examples of electrolytic hydrogenation. Not only can the reduction to aniline be accomplished effectively, but also, by suitable control of the potential and the acidity of the solution, together with proper choice of electrodes, it is possible to obtain large yields of any one of the intermediate products, azoxybenzene, azobenzene, and hydrazobenzene, each representing a step in the reduction of nitrobenzene. Electrolytic oxidations at the anode are also important.

REFERENCES

Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1943.

MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939.

Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., New York, 1942.

Dole, "Experimental and Theoretical Electrochemistry," McGraw-Hill Book Co New York, 1935.

Kraus, "The Properties of Electrically Conducting Systems," Chemical Catalog Co., New York, 1932.

Creighton and Koehler, "Principles and Applications of Electrochemistry," John Wiley & Sons, New York, 1935.

PROBLEMS

1. A long glass tube is provided with electrodes at each end. When the tube is filled with 0.01 N NaCl, the resistance is 200 ohms. Estimate with the help of a graphical interpolation how many grams of $CaCl_2$ should be weighed out in a liter of solution so that the tube and solution will have a resistance of 5000 ohms.

Ans. 0.022g.

2. One hundred grams of sodium chloride is dissolved in 10,000 liters of water at 25° giving a solution which may be regarded in these calculations as infinitely dilute.

(*a*) What is the equivalent conductance of the solution?

(*b*) What is the specific conductance of the solution?

(*c*) This dilute solution is placed in a glass tube of 4 cm diameter provided with electrodes filling the tube and placed 20 cm apart. How much current will flow if the potential drop between the electrodes is 80 volts?

Ans. (*a*) 126.5 ohm^{-1}. (*b*) 2.16×10^{-5} ohm^{-1}. (*c*) 1.08×10^{-3} amp.

3. Ten amperes of current flowed for 1 hour through water containing a little sulfuric acid. How many liters of gas was formed at both electrodes at 27° and 740° mm pressure? *Ans.* 7.08 liters.

4. Determine the value of Λ_0 for lithium chloride from the following data at 25°.

Equivalents per liter	0.05	0.01	0.005	0.001	0.0005
Equivalent conductance	100.1	107.3	109.4	112.4	113.5

Ans. 115.0.

5. MacInnes and Dole electrolyzed 1.0 N potassium chloride at 25° between a silver anode and a silver chloride cathode and found that 113.51 g of water from the anode portion carried 7.9039 g of potassium chloride. The anode reaction is $Ag + Cl^- = AgCl + e$; the cathode reaction is $AgCl + e = Ag + Cl^-$. The middle portion, unchanged by the electrolysis, contained 7.1479 per cent by weight of potassium chloride. Calculate the number of equivalents of potassium ion which have migrated away from the solution surrounding the anode. The coulometer in the circuit gained 2.4835 g of silver from the deposition of silver. Calculate the transference number of potassium in 1.0 N KCl. *Ans.* 0.483.

6. The equivalent conductance of an infinitely dilute solution of ammonium chloride is 149.7, and the ionic conductances of the ions OH^- and Cl^- are 198.0 and 76.3, respectively. Calculate the equivalent conductance of ammonium hydroxide at infinite dilution. *Ans.* 271.4.

7. The following table gives the specific conductance of a solution of hydrochloric acid to 100 ml of which have been added various amounts of a 7 N solution of sodium hydroxide. If the dilution effect of the small amount of hydroxide solution added is neglected, what is the normality of the hydrochloric acid solution?

NaOH, ml	0.28	0.92	1.38	2.16
Conductance	0.0306	0.0166	0.0154	0.0288

Ans. 0.0804 N.

8. (*a*) What is the resistance of a glass cell which is 5 cm in diameter with electrodes 10 cm apart when filled with 0.01 N $CuSO_4$ which has an equivalent conductance of 83.1 ohm^{-1}?

(*b*) What is the resistance of the same cell when filled with water which contains 0.1 g of $CuSO_4$ per liter?

9. Estimate the specific conductance at 25° of water which contains 70 parts per million by weight of magnesium sulfate.

10. From the values of the equivalent conductance at different concentrations for aqueous nitric acid at 18°, determine the equivalent conductance of an infinitely dilute solution at 18°.

Conc. (Milliequivalents per liter)	*Equivalent Conductance*
2.0	371.2
10.0	365.0
50.0	353.7
100.0	346.4

11. State quantitatively what the chemical changes will be at the cathode and the anode when a current of 1 ampere is passed for 20 minutes through the following solutions:

	(*a*)	(*b*)	(*c*)
Cathode	Graphite	Mercury	Silver
Solution	H_2SO_4	$ZnCl_2$	$FeCl_3$
Anode	Platinum	Zinc	Silver

12. A 6-volt storage battery operates two 4-ampere lamps in parallel for 5 hours. How many grams of lead is oxidized? If 5 per cent of the energy goes into light and 95 per cent into heat, how many calories of heat is given off by the lamps?

13. A solution of hydrochloric acid was electrolyzed in a transference cell between platinum electrodes. The cathode compartment contained 0.177 g of chloride ions before the electrolysis and 0.163 g afterwards. A silver coulometer in series had a deposit of silver equivalent to 0.0825 g of chloride ions. What are the transference numbers of H^+ and Cl^-?

14. A glass tube having a uniform cross section of 1 sq cm was partly filled with 0.01 *N* hydrochloric acid, and a solution of an inert electrolyte was poured in on top so as to give a boundary. When a constant current of 10 milliamperes was passed through for 200 seconds, the hydrogen ions moved 17 mm toward the cathode, as shown by a color indicator for hydrogen ions. Calculate the transference number of the hydrogen ions in 0.01 *N* hydrochloric acid.

15. At 25° the equivalent conductance at infinite dilution Λ_0 of sodium monochloroacetate is 89.8. Calculate Λ_0 at 25° for monochloroacetic acid.

16. Calculate the equivalent conductance at infinite dilution of ammonium sulfate at 55°.

17. The following table gives the specific conductance of a solution of hydrochloric acid, to 100 ml of which have been added various amounts of an 8 *N* solution of sodium hydroxide. If the dilution effect of the small amount of hydroxide solution added is neglected, what is the normality of the hydrochloric acid solution?

NaOH, ml	0.32	0.92	1.56	2.34
Conductance, Λ	0.0322	0.0186	0.0164	0.0296

18. An electrolytic cell containing a cadmium sulfate solution was subjected to various applied potentials, and the corresponding currents were measured. The results were as follows:

E (volts)	0.5	1.0	1.5	1.8	2.0	2.2	2.4	2.6	3.0
I (ampere)	0.002	0.004	0.006	0.007	0.008	0.028	0.069	0.110	0.192

What is the decomposition potential of cadmium sulfate?

---

19. One milligram of potassium chloride is dissolved in 1 liter of water at 25° giving a solution which may be regarded as infinitely dilute.

(*a*) What is the equivalent conductance?

(*b*) What is the specific conductance?

(*c*) This solution is placed in a glass tube of 2 cm diameter provided with electrodes, which fill the tube, and placed 10 cm apart. How much current will flow if the potential drop between the electrodes is 50 volts?

20. A sample of water from a large pool had a resistance at 25° of 9200 ohms when placed in a certain conductance cell. When filled with 0.020 *M* KCl the cell had a resistance at 25° of 85 ohms. Five hundred grams of sodium chloride was dissolved in the pool, which was then thoroughly stirred. A sample of this solution gave a resistance of 7600 ohms. With the help of graphical interpolation calculate the number of liters of water in the pool.

21. What is the molar conductance of metallic mercury at 0°?

22. What are the probable products of electrolysis at each electrode when a current of electricity is passed through the following cells:

(*a*) An aqueous solution of copper sulfate with copper electrodes.

(*b*) An aqueous solution of ferrous sulfate with graphite electrodes.

(*c*) An aqueous solution of lithium iodide with mercury electrodes.

(*d*) A solution of sodium iodide in acetone with platinum electrodes.

23. A glass tube 4 cm in diameter and 30 cm long is closed at each end with a sheet silver electrode and filled with 0.01 *N* silver nitrate. Sixty volts are applied.

(*a*) How much current flows? (*b*) How many degrees will the temperature of the solution rise in 10 minutes, if it is assumed that the heat capacity of the solution is nearly 1 cal deg^{-1} per milliliter and that all the heat is taken up by the solution?

24. (*a*) How many ampere-hours of electricity are required to refine by electrolysis 453 g (1 lb) of copper, removing it from the impure anode and depositing it in a pure state on the cathode?

(*b*) If the potential drop across the electrolytic cell is 5 volts, how much will the electricity cost at 1 cent per kilowatt-hour?

25. The silver nitrate solution from the central compartment of a transference cell weighed 36.5 g and was titrated with 32.7 ml of ammonium thiocyanate solution, 1 ml of which was equivalent to 0.0085 g of silver nitrate. The solution from the cathode compartment weighed 43.17 g and required 29.4 ml of ammonium thiocyanate solution. A silver coulometer in series with the transference cell had a deposit of 0.0994 g of silver. What are the transference numbers of the silver ion and the nitrate ion?

26. A current of 0.01 ampere is passed through an 0.01 molar solution of lithium chloride at 25° for 100 seconds using silver electrodes. (*a*) How much, if any, will each electrode gain in weight? (*b*) Estimate the number of equivalents of chloride ion which will be found in the 100 ml of solution which surrounds the anode.

27. In 0.1 *N* Na_2SO_4 the transference number of the sodium ion is 0.383. If a suitable boundary is made in a uniform glass tube 18 mm in diameter, and 0.02 ampere is passed through the tube for 5 minutes, how far will the boundary of sodium ions move toward the cathode?

28. What is the specific conductance at 0° of a solution containing 0.1 g of $CaSO_4$ per liter? (Λ is practically equal to Λ_0.)

29. Sketch a curve for the conductometric titration of a weak acid by a strong base.

---

30. The absolute velocities of ions have been determined by direct observation of a moving boundary. They may be calculated also from a knowledge of the equivalent conductance and the transference numbers. Imagine a solution containing c equivalents of a univalent electrolyte per 1000 ml in a 1-cm cube. Show that $(v_c + v_a)(c/1000)\,F = I$ where v_c and v_a are the velocities of the ions and I is the current; and that, since $I = L$, for a potential gradient of 1 volt per centimeter:

$$\Lambda = (v_c + v_a)F$$

Using the transference numbers, calculate the absolute velocity of the K^+ ion and the Cl^- ion at infinite dilution and 25°.

31. In determining the transference numbers of $Ba(HSO_4)_2$ in concentrated H_2SO_4 using platinum electrodes, the following are the analyses for a typical measurement expressed in grams of $BaSO_4$ per gram of solution:

Original	*Anode Compartment*	*Cathode Compartment*
0.02503	0.02411	0.02621

The solution had an average density of 1.90, the cathode compartment held 39 ml, and the anode compartment held 41 ml. During the experiment 4956 coulombs were transferred. What is the apparent transference number of Ba^{++} ion in the solution?

32. Outline methods by means of which the formation of a complex ion, such as $Cu(CN)_2^-$, might be determined in a solution containing both $CuCl_2$ and KCN, using (*a*) conductance measurements, (*b*) measurements of transference numbers.

CHAPTER XVI

ELECTROMOTIVE FORCE

Galvanic Cells. The behavior of electrolytes during the passage of an electric current through them was studied in the preceding chapter. It was observed that electrons were supplied to the cathode by means of a dynamo or battery and then transferred to the positive ions which were in contact with it, thus neutralizing positive charges on the ions and frequently causing the ions to be discharged as neutral atoms or molecules. In a similar manner electrons were removed from the anode, thus leading to a reduction in the number of charges on the negative ions.

In the present chapter a study is made of the electromotive force which is produced by an excess of electrons at the anode and a deficiency at the cathode caused by the contact with ions which surround the electrodes. Usually a reaction may be divided into two parts: one an oxidation process involving a release of electrons and the other, a reduction process involving an absorption of electrons. The chemical tendency to release electrons at the anode feeds electrons into an electrically conducting electrode which is placed in the solution; and the chemical tendency of certain ions to absorb electrons causes electrons to be withdrawn from the cathode placed in the solution. Measurements of the voltage or electromotive force between two pairs of electrodes enable one to determine the relative tendency of the two reactions, one at the cathode and one at the anode, to release electrons. They enable one also to calculate the equilibrium constant of the over-all chemical reaction or to calculate the activities of the electrolytes which surround the electrodes. Frequently, concentrations are used instead of activities if the latter have not been determined. In some cases, particularly in dilute solutions or when great accuracy is not needed, they are used interchangeably.

Galvanic cells for the production of electricity from chemical reactions have been known since 1800, when Volta described his electric pile. One of the oldest and simplest cells consists of a zinc electrode immersed in zinc sulfate and a copper electrode immersed in copper sulfate, the two solutions being separated from each other by a porous cup, or, in certain types of vertical cells, by gravity. The electromotive

force of such a cell is about 1 volt, the zinc electrode being negative and the copper positive.

The operation of the cell may be understood with the help of **Fig. 108.** Each electrode is bathed in a solution of its ions, and there is an equilibrium at each as indicated by the reactions:

$$Zn^{++} + 2e \rightleftharpoons Zn$$

$$Cu^{++} + 2e \rightleftharpoons Cu$$

The copper ions, however, attract their valence electrons with greater force than do the zinc ions; that is, copper is less easily ionized than zinc. In the competition for electrons, copper ions are more effective than zinc ions and they remove electrons from the copper electrode. When the wire between the two electrodes is disconnected, the reactions stop, but, as long as there is electric connection between the two electrodes, electrons are removed from the copper electrode by the reaction $Cu^{++} + 2e \rightarrow Cu$, and electrons are provided at the zinc electrode by the reaction $Zn \rightarrow Zn^{++} + 2e$. Faraday's law applies, and the following phenomena take place: (1) 1 gram equivalent of zinc atoms releases two electrons per atom, and goes into solution as zinc ions; (2) 6.02×10^{23} electrons, which are equivalent to 96,500 coulombs of electricity, travel along the wire from the zinc electrode to the copper electrode; (3) 1 gram equivalent of copper atoms is deposited by the addition of electrons to copper ions which collide with the negative copper electrode.

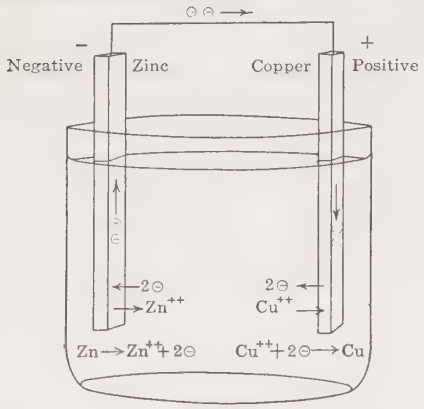


FIG. 108. Illustration of a typical galvanic cell showing the chemical reactions occurring at the electrodes.

As long as the circuit is closed, these reactions go on, consuming zinc and depositing copper until either the zinc or the supply of copper ions is exhausted. If the circuit is left open, the chemical action ceases, except for diffusion of the ions and local action, which is due to impurities in the zinc acting to give tiny local cells. This action which consumes the zinc on open circuit can be greatly reduced by using very pure zinc or by coating or amalgamating the surface of the zinc with mercury. This procedure gives a coating over the impurities and does

not change the voltage appreciably, because a saturated solution of zinc in mercury possesses practically the same potential as pure zinc.

Many other galvanic cells have been devised, but the zinc and copper cell serves to illustrate the general principle by which electricity can be furnished from chemical reactions. Several cells of the same kind can be arranged in series to give a *battery* of higher voltage, which is equal to the sum of the voltages of the individual cells. Although electricity can be produced much more cheaply by operating a dynamo with mechanical power, the batteries have the advantage of portability, and two types have survived severe economic competition. The lead storage battery is used for starting automobiles, and the Leclanché dry cell of zinc and ammonium chloride is used in flashlights, portable radio sets, and hearing aids.

Standard Cells. The cadmium cell shown in **Fig. 109** is the accepted standard for measuring voltages. Platinum electrodes are sealed through the bottoms of two glass tubes connected by a horizontal arm.

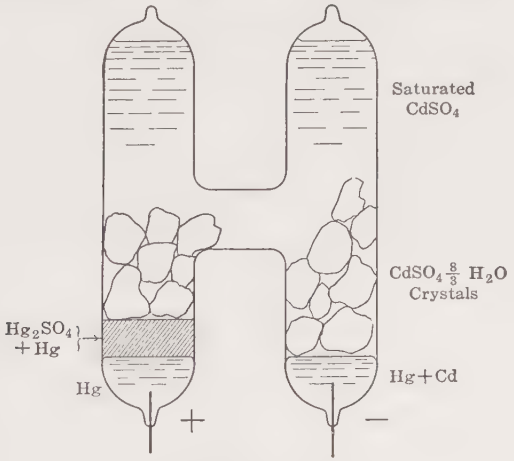


Fig. 109. Weston or cadmium sulfate standard cell—used as a reference for measuring voltage.

One tube holds a cadmium amalgam, containing 10 to 13 per cent of cadmium in mercury, and the other contains pure mercury on which floats a paste of mercury and mercurous sulfate. The cell is then filled with a concentrated solution of cadmium sulfate or a saturated solution containing an excess of solid crystals of $CdSO_4 \cdot \frac{8}{3}H_2O$. The latter is the accepted standard, but the former has a lower temperature coefficient which renders it more convenient for laboratory use.

This cell is reversible, and, unless abnormally large currents are drawn, the voltage remains constant. When it operates spontaneously,

cadmium goes into solution as cadmium ions, and the electrons left by this ionization pass around the wire to the positive electrode, where mercurous ions take them up and deposit as mercury atoms. When the cell is opposed by a larger electromotive force, the current flows in the opposite direction with the result that cadmium is deposited, and mercury converted into mercurous ions. If the solution is saturated with respect to both cadmium sulfate and mercurous sulfate, a fixed concentration is maintained in spite of additions from the electrode or deposition on the electrode. In the unsaturated cell the concentration of the cadmium sulfate is so large that a small gain or loss does not change the concentration appreciably.

If the materials are carefully prepared and the cell made up according to specific directions,* the voltage will be 1.0186 at 20°, and this voltage will remain unchanged for years. For accurate work in electrochemistry, however, it is well to have the voltage checked occasionally against standard cells maintained at the U. S. Bureau of Standards in Washington or against secondary standards which, in turn, are calibrated at the Bureau of Standards. The voltage E of the saturated standard cadmium cell is 1.0186 absolute volts † at 20° and decreases 0.0000406 volt for each degree rise in temperature above 20°.

Reference Electrodes. The electromotive force or voltage of a cell is equal to the sum of the potentials of its two electrodes.‡ The *potential* of an electrode is the difference in potential between the electrode and the surrounding solution. It is determined by combining it with a *reference electrode* which has an arbitrarily assigned potential and measuring the total voltage between the two electrodes. All electrode potentials are assigned numerical values on the assumption that the potential of the standard hydrogen electrode (described on page 457) is zero.

The calomel electrode shown at the left of **Fig. 110** is a convenient reference electrode. It consists of pure mercury in the bottom of a vessel on which rests a paste of mercury and mercurous chloride (calomel). A solution of potassium chloride saturated with mercurous chloride makes electric contact, through a side arm provided with a porous plug or a loosely fitting ground-glass joint, with any solution in which the electrode is placed. Such a connecting solution is called a *salt bridge*. Sometimes a beaker of potassium chloride solution is placed

* Wolff and Waters, *Bur. Standards Bull.*, **3**, 623 (1907); **4**, 1 (1907); Vosburgh and Derr, *J. Chem. Education*, **18**, 87 (1941).

† The same cells calibrated before Jan. 1, 1948, read 1.0183 international volts.

‡ There may be a small liquid-junction potential also (page 468). The present discussion assumes that this effect has been eliminated or that a correction has been applied.

between the calomel electrode and the electrode being measured, in order to minimize diffusion of mercurous ions into the solution. Electric connection with the mercury is made through a platinum wire fused to a copper wire and sealed through a glass tube.

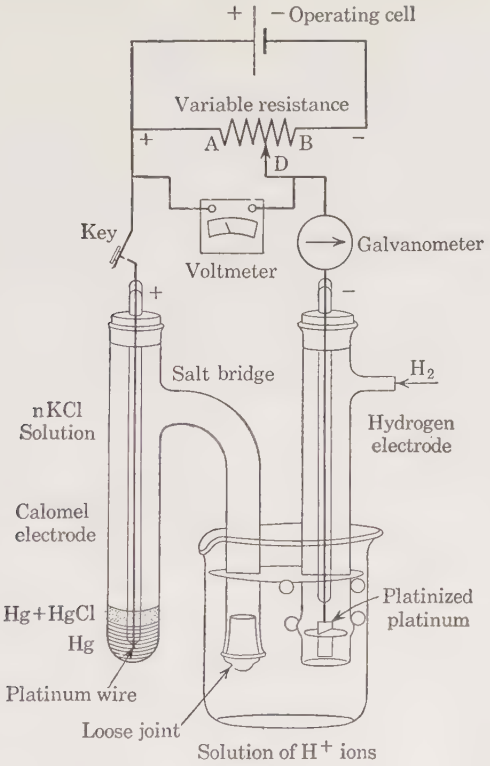


FIG. 110. Voltmeter—potentiometer with standard calomel electrode at left and hydrogen electrode at right.

The electrode shown at the right of Fig. 110 is a *hydrogen electrode* in which hydrogen gas at 1 atm bubbles over a platinized platinum electrode immersed in a solution of hydrogen ions. When the hydrogen ions are at an effective concentration or activity of unity, the electrode is arbitrarily assigned a value of 0.000 volt and used as the standard to which all other potentials are referred.

The normal calomel electrode contains a molar solution of potassium chloride and has a voltage of −0.2801 at 25° with reference to the standard hydrogen electrode. The saturated calomel cell contains saturated potassium chloride and has a potential of −0.246 with reference to the standard hydrogen electrode. It is used sometimes in special cases

where it is desired to minimize the effect of other electrolytes, but it is inconvenient on account of the deposition of salts and because of a larger temperature effect.

Another reference electrode is the silver–silver chloride electrode. A silver wire or a deposit of silver on a platinum wire is partly covered with a thin coating of silver chloride, making it the anode in a chloride solution. The concentration of silver ions and chloride ions is fixed by the solubility of the silver chloride and maintained constant. The electrode is reversible with respect to both ions; that is, the ions can be deposited on or produced from the electrode by reversing the current. This electrode is more difficult to prepare, but it is especially valuable for certain measurements.

Voltage Measurement of Cells. A simple voltmeter cannot be used alone for measuring the electromotive force of a small cell, because the operation of the voltmeter causes some current to flow, thus initiating chemical changes at the electrodes and producing a different voltage. Furthermore, if any appreciable current is drawn, the internal resistance of the cell becomes a complicating factor.

To avoid these difficulties the electromotive force is measured by balancing against the cell a known voltage under conditions such that practically no current flows. A simple and practical method for measuring the electromotive force of a cell is shown in Fig. 110. The cell shown there consists of a hydrogen electrode and a calomel electrode. The two electrodes are connected to a variable, measured voltage through a galvanometer and key. The operating cell, of higher voltage than the cell to be measured, is connected to an adjustable rheostat AB. As the sliding contact is moved along the resistance, a smaller fraction AD of the total potential drop is intercepted, and the voltmeter connected across the resistance AD registers a lower voltage. The key is tapped momentarily as the sliding contact is moved until a position is found where the galvanometer is not deflected. At this position the voltage as read on the voltmeter is equal and opposite to that of the cell being measured. The cell is not altered by taking of the measurement, because practically no current flows through it, since the galvanometer, which is sensitive to very small currents, is kept at zero.

More accurate measurements of electromotive force are made with a *potentiometer*, the principle of which is shown in **Fig. 111.** As in the arrangement of Fig. 110, a measured potential is balanced against the cell through a galvanometer. In the potentiometer the opposing potential is not read on a voltmeter, but it is obtained accurately by connecting a known voltage across a uniform resistance AB. A sliding contact moves along the resistance, and the ratio of AD to AB measures the

fraction of the known potential drop which is picked off to oppose the voltage of the cell E being measured. The opposing voltage is supplied by a working cell C connected through an adjustable resistance R to the terminals of the uniform resistance AB. This resistance is divided into ten or more equal parts and marked with numbers corresponding

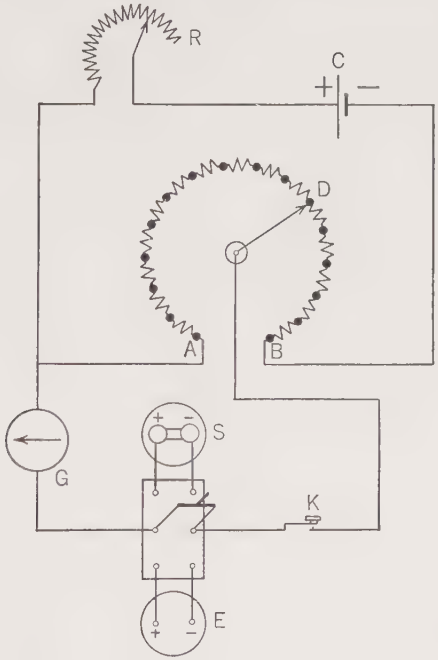


FIG. 111. The principle of the potentiometer in which the voltage of an unknown cell E is read directly from the electric resistances, after previous calibration with a standard cell S.

to their resistances. Each of these small units of resistance is itself divided into 1000 parts (not shown in Fig. 111) so that the potential drop opposing the cell E can be adjusted to 0.0001 of a unit and less.

In practice the double-throw switch is first connected to the standard cell S of known voltage, usually 1.0183 volt. The sliding contact is rotated to read 1.0183, and the key K is tapped momentarily as the external resistance R is adjusted, until the galvanometer G reads zero, showing that the voltage at 1.0183 is equal and opposite to that of the standard cell. When the voltage S is 1.0183, and the resistance is also 1.0183 units, each unit of resistance is equal to 1 volt, and the reading of the resistance is also the reading of the voltage. Then the switch is thrown to connect the potentiometer to a cell E, the voltage of which

is to be measured. The contact D is again rotated to a position such that the galvanometer shows no deflection when the circuit is closed by the tapping key. Then the number on the potentiometer gives directly in volts the electromotive force of the cell E.

Reversible Cells. The cadmium–mercury cell and the copper–zinc cell are examples of reversible cells which can be brought back to their original state after operating a while, by application of a higher opposing voltage and passage of current through the cell in the opposite direction. In irreversible cells the original conditions cannot be restored by reversing the current, because some of the material involved has been removed, as, for example, when a gas is evolved or a precipitate formed. If more than an infinitesimal quantity of current is passed through the cell, some of the electric energy will be converted into heat and lost, so that the cell cannot be completely reversed unless extra external energy is applied. Under these conditions the work done will not be the maximum work which might have been obtained. This maximum electrical work is definite, and it is of great value in thermodynamical calculations. The measurements of irreversible cells are not significant in theoretical calculations, but they may be of value in practical measurements. Sometimes it is possible to determine from the experimental behavior of a cell whether or not it is reversible. For example, if mechanical agitation produces marked unsteadiness in voltage, or if the cell does not return to the same voltage after a larger current is allowed to pass momentarily, the cell probably is not reversible.

The maximum electrical work which can be done per gram equivalent of material used in a galvanic cell can be calculated by multiplying the voltage by 96,500 coulombs, provided that the voltage is measured with a potentiometer and sensitive galvanometer using a negligible current of perhaps a millionth of an ampere or less.

Relation between Chemical Energy and Electric Energy. In earlier chapters we have seen that at constant temperature and pressure the changes in a chemical system can be measured in terms of the maximum work, other than pressure–volume work, which can be done, that is, the change in free energy ΔF.

When a cell operates reversibly at constant pressure and temperature, the electrical work obtained per gram atom is nFE, where n is the valence change, F is the faraday or 96,500 coulombs, and E is the voltage or electromotive force of the cell. This maximum electrical work in joules may be converted into calories by dividing by 4.1840. Then F corresponds to 23,060 cal per volt. In addition to the electrical work, some pressure–volume work may be done also, as, for example, when a gas is evolved by the operation of the cell. This pressure–volume work

at constant pressure done on or by the atmosphere is not included in the free-energy change ΔF. Neither is it included in the maximum electrical work. Then,

$$\Delta F = -nFE \tag{1}$$

According to this important equation, the electrical work done in a cell at constant temperature and pressure is equal to the decrease in free energy, whether or not there is a change in volume.

Example 1. The voltage of a copper–copper sulfate zinc sulfate–zinc cell is 1.107 volts. What is the free-energy change involved when the cell consumes a mole of zinc?

$$\Delta F = -nFE = -2 \times 96{,}500 \times 1.107 = -213{,}650 \text{ joules per mole}$$

$$= -\frac{213{,}650}{4.184} = -51{,}063 \text{ cal per mole}$$

The relation between the heat of reaction and the electromotive force of a cell may be obtained from the Gibbs–Helmholtz equation,

$$\Delta F - \Delta H = T\left(\frac{\partial(\Delta F)}{\partial T}\right)_p \tag{2}$$

which was derived on page 161.

Substituting for ΔF its equivalent $-nFE$, we have

$$\Delta F = -nFE = \Delta H - nFT\frac{\partial E}{\partial T}$$

$$\Delta H = -nFE + nFT\frac{\partial E}{\partial T} \tag{3}$$

This equation expresses the electromotive force of a reversible cell in terms of the temperature coefficient of the cell and the heat of the chemical reaction occurring within the cell. It may be used to calculate the heat of reaction from the measured voltage and the temperature coefficient of voltage. Since the precision of electrical measurements is, in general, greater than that of thermal measurements, this indirect method often gives results which are more accurate than the calorimetrically determined values.

As discussed on page 107, ΔH is the heat of reaction q_p when the reaction takes place in a beaker or calorimeter at constant pressure and temperature, and no work other than pressure–volume work is done by the system. It is not the same as the heat of reaction q_p when the same reaction takes place *reversibly* in the cell at constant pressure and temperature. Under these conditions the cell does electrical work, and, although

ΔH is the same because the initial and final states are the same, the values of q_p are quite different. The heat absorbed q_p when the cell operates reversibly is $T\Delta S$, and

$$T\Delta S = \Delta H - \Delta F = nFT\frac{\partial E}{\partial T} \tag{4}$$

Example 2. Calculate the value of ΔH for the reaction of the cadmium–silver chloride cell at 25° from the fact that the electromotive force is 0.67533 volt and the temperature coefficient is −0.000650 volt per degree.

$$\Delta H = -\frac{nF}{4.1840}\left(E - T\frac{\partial E}{\partial T}\right) = -\frac{2 \times 96{,}500}{4.1840}(0.67533 + 298.1 \times 0.000650)$$

$$= -40{,}090 \text{ cal}$$

Calorimetric measurements on the evolution of heat give $\Delta H = -39{,}530$ cal.

Further examples are given in Table I. The agreement between the calculated and the experimental values of ΔH is entirely satisfactory.

TABLE I

Experimental Verification of the Gibbs–Helmholtz Equation

Cell	E, volts	$\partial E/\partial T$, volts/degree	ΔH, equation 3	ΔH (obs.) calorimeter, cal	$-\frac{\Delta F, nFE}{4.1840}$
Zn, $ZnCl_2$(0.555m), AgCl, Ag(0°)	1.015	−0.000402	−51,990	−52,050	−46,830
Cd, $CdCl_2 \cdot 2\frac{1}{2}H_2O$ (satd.), AgCl, Ag(25°)	0.67533	−0.00065	−40,080	−39,530	−31,160
Cd, $CdCl_2 \cdot 2\frac{1}{2}H_2O$ (satd.), $PbCl_2$, Pb(25°)	0.18806	−0.00048	−15,250	−14,650	−8,670
Pb, $Pb(C_2H_3O_2)_2$ (0.555m), $Cu(C_2H_3O_2)_2$ (satd.), Cu(0°)	0.4764	+0.000385	−16,900	−17,530	−21,990

A comparison of the last two columns is particularly interesting. The electric energy in calories, $nFE/4.1840$, given in the last column, is the change in free energy which accompanies the reaction, and it is a measure of the maximum useful work at constant pressure and temperature less the pressure–volume work.

For example, in the lead–copper cell $\Delta F = \Delta H - 4{,}460$ cal in agreement with a positive sign for the term $nFT(\partial E/\partial T)$.

In the special case where the voltage of the cell is independent of the temperature ($\partial E/\partial T = 0$), the heat of reaction and the free-energy change are equal. According to equation 4, when $nFT(\partial E/\partial T)$ has a positive sign, ΔH is greater than ΔF; that is, the heat evolved is greater than the maximum electrical work. When $\partial E/\partial T$ has a negative value, that is, the voltage decreases when the temperature is increased, ΔF is larger than ΔH, and more work can be obtained from the cell than corresponds to the heat evolved at constant pressure.

Classification of Cells. Several different types of electrodes and cells which find uses in the study of electrochemistry are shown in the summary which follows. A semicolon indicates a contact between two different phases. The symbol Pt indicates an inert electrode like platinum.

Types of Electrodes and Electrode Reactions

1. Metal, metal ion	$Cu; Cu^{++}$
2. Inert electrode, nonmetal in solution, ion	$Pt; I_2\ (s), I^-$
3. Inert electrode, ions of different valence	$Pt; Fe^{+++}, Fe^{++}$
4. Inert electrode, gas, ion	$Pt, H_2; H^+$
5. Inert electrode, neutral solutes in different states of oxidation	$Pt; C_6H_4(OH)_2, C_6H_4O_2$
6. Amalgam electrode, ion	$(Cd + Hg); Cd^{++}$
7. Electrode, insoluble salt or oxide, ion	$Ag, AgCl; Cl^-$

Any of these electrodes may be combined with any other to give a cell, the electromotive force of which is equal to the algebraic sum of the potentials of the two electrodes. If precipitation or chemical action occurs when the solutions surrounding the two electrodes are mixed, they must be kept separate with a salt bridge of potassium chloride or other suitable solution which permits the passage of an electric current.

When the electrodes are combined in such a way as to give a liquid junction, that is, a contact between two different solutions, a small potential is created at such a liquid junction (page 468). It may be rendered nearly negligible by interposing a salt bridge of potassium chloride. The presence or absence of such a liquid junction is important in handling problems of electrochemistry.

The cells may be classified as follows:

A. Cells with liquid junctions:

1. Different electrodes — $Zn; Zn^{++}; Cu^{++}; Cu$
2. Concentration cells — $Pt, H_2; HCl\ (a = 1); HCl\ (a = 0.1); H_2, Pt$

The activities a, or effective concentrations, of the electrolytes are given in parentheses.

B. Cells with the junction potential practically eliminated by means of a salt bridge, indicated by the sign ||:

1. Different electrodes	$Zn; Zn^{++} \| \| Cu^{++}; Cu$
2. Concentration cells	$Pt, H_2; H^+ (a = 0.1) \| \| H^+ (a = 0.01); H_2, Pt$

Sometimes the junction potential is corrected by a calculation.

C. Cells without liquid junction:

1. Different electrodes	$Pt, H_2; H^+, Cl^-; Cl_2, Pt$
2. Concentration cell of metal	$(Hg + 10\%\ Cd); Cd^{++}; (Hg + 1\%\ Cd)$

Cells with liquid junctions between different electrolytes cannot be given exact thermodynamic treatment and are to be avoided for such theoretical studies. However, the cells in which the liquid-junction potentials have been practically eliminated by a salt bridge are used widely in the determination of the activity of ions as, for example, hydrogen ions.

Electrochemical Conventions. The chemical equilibrium involving electrolytes is closely connected with the voltage of the corresponding galvanic cell. Either can be calculated from the other, and, in practice, a table of standard electrode potentials for the different ions is very useful for calculating the free-energy changes and determining the chemical equilibrium constants. The following conventions regarding the sign and the arrangement of the two electrodes facilitate these calculations.

1. A substance is oxidized when it loses electrons; and it is reduced when it gains electrons. It is customary in electrochemistry to emphasize the oxidation reactions although it must be realized that, in every reaction involving electrons, reduction is taking place simultaneously with oxidation.

For each of the oxidation reactions there is a corresponding electrode and a definite electrode potential. A few examples are given in Table II.

There is a dynamic equilibrium between zinc and zinc ions; Zn atoms tend to go into solution with the loss of electrons to the electrode, and Zn^{++} ions tend to take electrons from the electrode with the formation of Zn atoms. The potential of the zinc electrode involves a balance between these two tendencies and depends in part on the number of collisions per second per square centimeter of zinc ions on the metallic zinc. Again, we may consider an inert platinum wire immersed in a solution containing a mixture of ferrous and ferric ions. The potential

of the wire will depend on the ratio of the two, the Fe^{++} ions tending to give electrons to the wire and the Fe^{+++} ions tending to take them away. Accordingly, in defining an electrode potential it is necessary to specify a definite concentration of reducing or oxidizing ions.

TABLE II

Typical Oxidation Reactions and Oxidation Electrode Potentials

Oxidation by Loss of Electrons		Electrode Reaction	Electrode	Standard Oxidation Electrode Potential, E^0, volts
Reduced Form	Oxidized Form			
Zinc	Positive zinc ions	$\frac{1}{2}Zn = \frac{1}{2}Zn^{++} + e$	$Zn; Zn^{++}$	0.762
Cadmium	Positive cadmium ions	$\frac{1}{2}Cd = \frac{1}{2}Cd^{++} + e$	$Cd; Cd^{++}$	0.408
Hydrogen	Positive hydrogen ions	$\frac{1}{2}H_2 = H^+ + e$	$Pt, H_2; H^+$	0.000
Positive ferrous ions	Positive ferric ions	$Fe^{++} = Fe^{+++} + e$	$Pt; Fe^{++}, Fe^{+++}$	−0.771
Negative chloride ions	Chlorine	$Cl^- = \frac{1}{2}Cl_2 + e$	$Pt, Cl_2; Cl^-$	−1.358

2. The standard electrode potential E^0 is defined as the potential which exists when the electrode is immersed in a solution of the ions at unit activity ($a = 1$).*

3. All electrode potentials are referred to the standard hydrogen electrode (1 atm of hydrogen with hydrogen ions at unit activity) which is arbitrarily assigned an electrode potential of zero. $E^0_{Pt,\,H_2;\,H^+} = 0$. If there is a greater tendency toward oxidation, that is, toward loss of electrons in an electrode reaction than in the reference reaction, $\frac{1}{2}H_2 = H^+ + e$, the corresponding electrode is given a positive sign,† and, if there is a lesser tendency toward oxidation than in the case of hydrogen, the electrode is given a negative sign. The electrode with the largest positive oxidation potential is placed at the top of a table of electrode potentials, and the others are arranged in order of decreasing oxidation potentials.

4. The reduced form of any metal or ion at unit activity will reduce the oxidized form of any metal or ion at unit activity which lies below it in the

* The method of determining activities is given on pages 469 and 682. Usually a concentration of 1 mole per 1000 g differs considerably from an activity of unity.

† In former editions of this book the electrode potentials were given as reduction potentials rather than oxidation potentials, and the signs were reversed. The electrodes above hydrogen such as zinc were given negative values. Although there are practical arguments for such a practice, the change has been made in the interest of greater uniformity among different authors. No fundamental change of electrochemical conventions is involved.

table of E^0 values, that is, which has a less positive oxidation electrode potential. The magnitude of the electrode potential is a measure of the ease with which the element or ion will lose its electrons; thus, if E^0 for Zn; Zn^{++} is 0.762, and E^0 for Pt; Fe^{++}, Fe^{+++} is -0.771, the reduced form of the Zn; Zn^{++} pair which is zinc will reduce the oxidized form of the Fe^{++}; Fe^{+++} ion pair, which is ferric ion, and produce ferrous ion. The zinc loses its electrons more easily than does ferrous ion, and so the ferric ions acquire electrons from the zinc. The zinc is oxidized to zinc ions, and the ferric ions become reduced to ferrous ions. The reaction is $\frac{1}{2}Zn + Fe^{+++} = \frac{1}{2}Zn^{++} + Fe^{++}$, and it takes place spontaneously.

The tables of electrode potentials are useful not only for qualitative predictions but for quantitative calculations of the equilibrium. To carry out these calculations without ambiguity, it is necessary to adopt further conventions in order to correlate the electromotive force of a cell with the chemical reaction occurring in the cell.

5. The voltage or electromotive force of a cell is equal to the algebraic sum of the potentials of the two electrodes; and the cell reaction is equal to the algebraic sum of the two electrode reactions. A galvanic cell has two electrodes: an anode which takes up electrons from the oxidation reactions in the surrounding solution and passes them into the connecting wire, and a cathode which takes these electrons from the circuit and gives them to ions or atoms which thereby become reduced.

6. Galvanic cells are arbitrarily written with the anode (the electrode which has an excess of electrons) at the left. The electromotive force of the cell is then arbitrarily assigned a positive value.

Oxidation is then occurring at the left where the electrons are released either by the formation of positive ions, by the increase in valence of positive ions or by the discharge of negative ions. The electrons then pass through an external connecting wire from the anode at the left to the cathode at the right, where they are absorbed by the discharge of positive ions or by some other reducing reaction.

If the cell should happen to be written with the negative electrode at the right instead of at the left, the electromotive force of the cell is then given a negative sign.

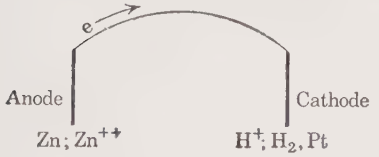
7. The cell reaction is split into two electrode reactions. The oxidation part which liberates electrons is written as the reaction of the left electrode, and the reduction part which absorbs electrons is written as the reaction of the right electrode.

Thus in the reaction $Zn + Cu^{++} = Zn^{++} + Cu$, $Zn = Zn^{++} + 2e$ is the oxidation reaction occurring at the left electrode, and $Cu^{++} + 2e = Cu$ is the reduction reaction occurring at the right electrode.

8. If the electromotive force of the cell is positive (that is, the left electrode is the anode), *the cell reaction is spontaneous; and, if the cell reaction as written is spontaneous, ΔF has a negative value, the electromotive force of the cell E is positive, and the electrode at the left is the anode.*

These relations follow directly from conventions 6 and 7; the fundamental equation, $\Delta F = -nEF$; and the generalization that spontaneous reactions at constant temperature and pressure have a negative value of ΔF.

A few examples will serve to illustrate these conventions.



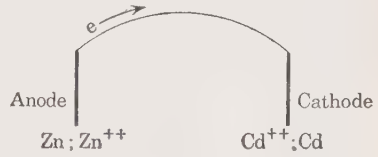
$E^0_{Zn;\,Zn^{++}} = 0.762 \quad E^0_{H^+;\,H_2,\,Pt} = 0.0$

$E^0 = 0.762 + 0.0 = 0.762$

Left $\frac{1}{2}Zn = \frac{1}{2}Zn^{++} + e$ = oxidation

Right $H^+ + e = \frac{1}{2}H_2$ = reduction

Cell $\frac{1}{2}Zn + H^+ = \frac{1}{2}Zn^{++} + \frac{1}{2}H_2$



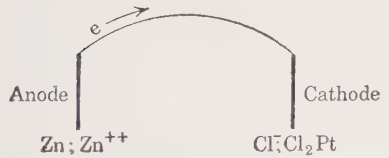
$E^0_{Zn;\,Zn^{++}} = 0.762 \quad E^0_{Cd^{++};\,Cd} = -0.402$

$E^0 = 0.762 + (-0.402) = 0.360$

Left $\frac{1}{2}Zn = \frac{1}{2}Zn^{++} + e$ = oxidation

Right $\frac{1}{2}Cd^{++} + e = \frac{1}{2}Cd$ = reduction

Cell $\frac{1}{2}Zn + \frac{1}{2}Cd^{++} = \frac{1}{2}Zn^{++} + \frac{1}{2}Cd$



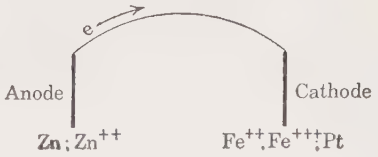
$E^0_{Zn;\,Zn^{++}} = 0.762 \quad E^0_{Cl^-;\,Cl_2,\,Pt} = 1.358$

$E^0 = 0.762 + 1.358 = 2.120$

Left $\frac{1}{2}Zn = \frac{1}{2}Zn^{++} + e$ = oxidation

Right $\frac{1}{2}Cl_2 + e = Cl^-$ = reduction

$\frac{1}{2}Zn + \frac{1}{2}Cl_2 = \frac{1}{2}Zn^{++} + Cl^-$



$E^0_{Zn;\,Zn^{++}} = 0.762 \quad E^0_{Fe^{++},\,Fe^{+++};\,Pt} = 0.771$

$E^0 = 0.762 + 0.771 = 1.533$

Left $\frac{1}{2}Zn = \frac{1}{2}Zn^{++} + e$ = oxidation

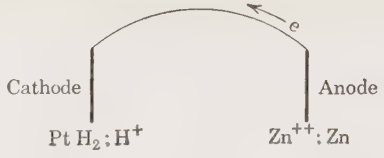
Right $Fe^{+++} + e = Fe^{++}$ = reduction

$\frac{1}{2}Zn + Fe^{+++} = \frac{1}{2}Zn^{++} + Fe^{++}$

In these four examples the anode is written at the left, E^0 has a positive value, ΔF has a negative value, and the cell reaction as written is spontaneous.

In the following example the anode is written at the right contrary to the conventions. Then E has a negative value, ΔF has a positive

value, and the cell reaction $\frac{1}{2}H_2 + \frac{1}{2}Zn^{++} = H^+ + \frac{1}{2}Zn$ cannot take place spontaneously.



$$E^0_{Pt,\,H_2;\,H^+} = 0 \qquad E^0_{Zn^{++};\,Zn} = -0.762$$

$$E^0 = 0 + (-0.762) = -0.762$$

Table of Standard Oxidation Potentials. In Table II a few electrode potentials were given to illustrate their application. Many additional ones are included in Table III.

The electrode at the left is, of necessity, written in the order *electrode*: *ions* and has the electrode potential given in the table (if the ions are at unit activity). The electrode at the right, however, has to be written in the order *ions*:*electrode*, and its sign as given in Table III must be reversed.*

The values of E^0 are obtained by making electromotive-force measurements at several dilutions and extrapolating a function of the voltage to infinite dilution, as explained on page 682. Considerable ingenuity and care are necessary in obtaining these values of E^0.

In practical laboratory work the normal calomel cell is usually used as a reference electrode rather than the standard hydrogen electrode. If an electrode potential is measured against the normal calomel cell at 25°, it is necessary to subtract 0.280 volt in order to obtain the potential which the electrode would have if measured against the standard hydrogen electrode.

It should be emphasized that the sign of an *electrode potential* is determined by reference to the standard hydrogen electrode. If it is positive, the reduced form will reduce hydrogen ion spontaneously to hydrogen; and, if it is negative, the reduced form will not reduce hydrogen ion—the ions being at unit activity in all cases.

The sign of an electrode in a galvanic *cell*, however, is not dependent on the hydrogen electrode but is determined by the other electrode

* The important convention to observe is that the electrodes recorded in Table III are standard oxidation electrodes written in the order, electrode:ions, regardless of whether positive or negative ions are involved. Thus, when $Zn:Zn^{++}$ is the left electrode, the potential is +0.762 as given in the table, but, when the electrode is placed at the right, it must be read Zn^{++}:Zn and its potential is −0.762. Some books record the standard reduction potentials instead of oxidation potentials and give Zn^{++}; Zn. $E^0 = -0.762$.

TABLE III

Standard Oxidation Electrode Potentials[1]

All ions are at unit activity. The potential is then designated by E^0. The temperature is 25°.

Electrode (Anode) (Oxidizing Electrode)	E^0 in absolute volts (Standard hydrogen electrode = 0)	Electrode Reaction (Anode Reaction) (Oxidation Reaction)
$Li; Li^+$	3.025	$Li = Li^+ + e$
$K; K^+$	2.923	$K = K^+ + e$
$Na; Na^+$	2.713	$Na = Na^+ + e$
$Zn; Zn^{++}$	0.762	$\frac{1}{2}Zn = \frac{1}{2}Zn^{++} + e$
$Fe; Fe^{++}$	0.440	$\frac{1}{2}Fe = \frac{1}{2}Fe^{++} + e$
$Pt; Cr^{++}; Cr^{+++}$	0.41	$Cr^{++} = Cr^{+++} + e$
$Cd; Cd^{++}$	0.402	$\frac{1}{2}Cd = \frac{1}{2}Cd^{++} + e$
$Tl; Tl^+$	0.336	$Tl = Tl^+ + e$
$Pb, PbBr_2\ (s); Br^-$	0.280	$\frac{1}{2}Pb + Br^- = \frac{1}{2}PbBr_2 + e$
$Co; Co^{++}$	0.277	$\frac{1}{2}Co = \frac{1}{2}Co^{++} + e$
$Ni; Ni^{++}$	0.250	$\frac{1}{2}Ni = \frac{1}{2}Ni^{++} + e$
$Ag, AgI\ (s); I^-$	0.151	$Ag + I^- = AgI + e$
$Sn; Sn^{++}$	0.140	$\frac{1}{2}Sn = \frac{1}{2}Sn^{++} + e$
$Pb; Pb^{++}$	0.126	$\frac{1}{2}Pb = \frac{1}{2}Pb^{++} + e$
$Pt, D_2; D^+$	0.0034	$\frac{1}{2}D_2 = D^+ + e$
$Pt, H_2; H^+$	0.0000	$\frac{1}{2}H_2 = H^+ + e$
$Pt; Ti^{+++}, Ti^{++++}$	−0.04	$Ti^{+++} = Ti^{++++} + e$
$Ag, AgBr\ (s); Br^-$	−0.073	$Ag + Br^- = AgBr + e$
$Pt; Sn^{++}, Sn^{++++}$	−0.15	$\frac{1}{2}Sn^{++} = \frac{1}{2}Sn^{++++} + e$
$Pt; Cu^+, Cu^{++}$	−0.167	$Cu^+ = Cu^{++} + e$
$Ag, AgCl\ (s); Cl^-$	−0.2223	$Ag + Cl^- = AgCl + e$
Normal calomel electrode[2]	−0.2802	$Hg + Cl^- = \frac{1}{2}Hg_2Cl_2 + e$[3]
$Cu; Cu^{++}$	−0.345	$\frac{1}{2}Cu = \frac{1}{2}Cu^{++} + e$
$Pt, I_2\ (s); I^-$	−0.535	$I^- = \frac{1}{2}I_2 + e$
Pt; quinhydrone (s), H^+	−0.6996	$\frac{1}{2}C_6H_6O_2 = \frac{1}{2}C_6H_4O_2 + H^+ + e$
$Pt; Fe^{++}, Fe^{+++}$	−0.771	$Fe^{++} = Fe^{+++} + e$
$Hg; Hg_2^{++}$	−0.7988	$Hg = \frac{1}{2}Hg_2^{++} + e$
$Ag; Ag^+$	−0.799	$Ag = Ag^+ + e$
$Pt; Hg_2^{++}, Hg^{++}$	−0.910	$\frac{1}{2}Hg_2^{++} = Hg^{++} + e$
$Pt, Br_2\ (l); Br^-$	−1.0654	$Br^- = \frac{1}{2}Br_2\ (l) + e$
$Pt; Tl^+, Tl^{+++}$	−1.250	$\frac{1}{2}Tl^+ = \frac{1}{2}Tl^{+++} + e$
$Pt, Cl_2\ (g); Cl^-$	−1.358	$Cl^- = \frac{1}{2}Cl_2\ (g) + e$
$Pb, PbO_2; Pb^{++}$	−1.456	$\frac{1}{2}Pb^{++} + H_2O = \frac{1}{2}PbO_2 + 2H^+ + e$
$Pt; Ce^{+++}, Ce^{++++}$	−1.61	$Ce^{+++} = Ce^{++++} + e$
$Pt; Co^{++}, Co^{+++}$	−1.84	$Co^{++} = Co^{+++} + e$

[1] Most of these standard electrode potentials have been corrected to agree with those given by Latimer in "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, New York, 1938, page 294.

[2] The concentration of KCl is by definition 1 mole per liter.

[3] There is evidence that the mercurous ion is doubled, giving not Hg^+ but $\frac{1}{2}Hg_2^{++}$.

which comprises the galvanic cell. For example, a cadmium electrode is the anode and releases an excess of electrons when it is connected to a copper electrode in a cell; but the same cadmium electrode is the cathode which takes up electrons from the external circuit, when it is connected to a zinc electrode. The wire connected to the cadmium electrode then is negatively charged in a cadmium–copper cell, but it is positively charged in a cadmium–zinc cell.

The sign of the electromotive force of the cell involves a convention which has no significance as a laboratory measurement. According to convention 6, the electromotive force of the cell is arbitrarily defined as positive when the anode, the electrode with the greater tendency to give up electrons, is written on the page at the left.

Example 3. Give the cell reaction, and calculate the electromotive force and the free-energy change at 25° involved in the cell,

$$\mathrm{Zn};\ \mathrm{Zn^{++}}\ (a = 1)\|\mathrm{Cu^{++}}\ (a = 1);\ \mathrm{Cu}$$

The cell reaction is

$$\begin{array}{ll} \text{Left} & \tfrac{1}{2}\mathrm{Zn} = \tfrac{1}{2}\mathrm{Zn^{++}} + e \quad \text{(written as an oxidation)} \\ \text{Right} & \tfrac{1}{2}\mathrm{Cu^{++}} + e = \tfrac{1}{2}\mathrm{Cu} \quad \text{(written as a reduction)} \\ \hline & \tfrac{1}{2}\mathrm{Zn} + \tfrac{1}{2}\mathrm{Cu^{++}} = \tfrac{1}{2}\mathrm{Zn^{++}} + \tfrac{1}{2}\mathrm{Cu} \end{array}$$

$$\boldsymbol{E}^0 = \boldsymbol{E}^0_{\mathrm{Zn;\ Zn^{++}}} + \boldsymbol{E}^0_{\mathrm{Cu^{++};\ Cu}} = 0.762 + (+0.345) = 1.107$$

Because $\boldsymbol{E}$ of the galvanic cell has a positive value, it can be stated that the electrode at the left is the anode.

The free-energy change in going from the standard states for Zn and Cu^{++} to Cu and Zn^{++} is calculated as follows:

$$\Delta F^0 = -n\boldsymbol{F}\boldsymbol{E}^0 = -1 \times 96{,}500 \times 1.107 = -106{,}825 \text{ joules}$$

$$= -\frac{106{,}825}{4.1840} = -25{,}530 \text{ cal}$$

The electromotive force of a cell is the sum of the potentials of the two electrodes or half-cells, and the free energy of a reaction is the sum of the free energies of the electrode reactions. Multiples of the reaction may be taken without changing the potential, but the free energy is changed owing to the factor n in the equation $\Delta F = -n\boldsymbol{F}\boldsymbol{E}$.

Thus, if the reaction given in example 3 is written

$$\mathrm{Zn} + \mathrm{Cu^{++}} = \mathrm{Zn^{++}} + \mathrm{Cu}$$

$$\boldsymbol{E}^0 = 1.107 \quad \text{but} \quad \Delta F = -n\boldsymbol{F}\boldsymbol{E}^0 = -2 \times 96{,}500 \times \frac{1.107}{4.1840} = -51{,}060 \text{ cal}$$

The voltage is the same as for $\frac{1}{2}\mathrm{Zn} + \frac{1}{2}\mathrm{Cu^{++}}$, but the free energy is doubled because the chemical reaction involves twice as much material.

Since E for the cell in example 3 has a positive value, ΔF has a negative value, and, accordingly, metallic zinc will reduce copper ion to copper. Most students of chemistry would know that zinc will precipitate copper from solution, but there are many cases in which the direction of spontaneous reaction is not known, and it is then a simple matter to calculate whether the reaction as written is spontaneous or not.

Example 4. Write the cell which corresponds to the reaction,

$$\tfrac{1}{2}\mathrm{Cu}\ (s) + \tfrac{1}{2}\mathrm{Cl_2}\ (g\ 1\ \mathrm{atm}) = \tfrac{1}{2}\mathrm{Cu^{++}}\ (a = 1) + \mathrm{Cl^-}\ (a = 1)$$

$$\tfrac{1}{2}\mathrm{Cu}\ (s) = \tfrac{1}{2}\mathrm{Cu^{++}} + e \quad \text{(oxidation)}$$

$$\tfrac{1}{2}\mathrm{Cl_2}\ (g\ 1\ \mathrm{atm}) + e = \mathrm{Cl^-} \quad \text{(reduction)}$$

If the oxidation reaction is placed at the left and the reduction reaction at the right, the cell is written

$$\underset{\text{Oxidation}}{\mathrm{Cu}\ (s);\ \mathrm{Cu^{++}}\ (a = 1)} \parallel \underset{\text{Reduction}}{\mathrm{Cl^-}\ (a = 1);\ \mathrm{Cl_2};\ \mathrm{Pt}}$$

Calculate the voltage and the change in free energy of the reaction at 25°.

$$E^0 = E^0_{\mathrm{Cu;\ Cu^{++}}} + E^0_{\mathrm{Cl^-;\ Cl_2,\ Pt}} = -0.345 + (+1.358) = 1.013$$

$$\Delta F^0 = -nFE^0 = -1 \times \frac{96{,}500}{4.1840} \times 1.013 = -23{,}360\ \mathrm{cal}$$

Copper and chlorine will react spontaneously to give cupric ions and chloride ions.

Example 5. Will ferrous ion reduce iodine to iodide ion at 25° according to the reaction:

$$\mathrm{Fe^{++}} + \tfrac{1}{2}\mathrm{I_2}\ (s) = \mathrm{Fe^{+++}} + \mathrm{I^-}$$

$$\mathrm{Pt;\ Fe^{++},\ Fe^{+++}} \parallel \mathrm{I^-};\ \mathrm{I_2}\ (s),\ \mathrm{Pt}$$

$$E^0 = E^0_{\mathrm{Pt;\ Fe^{++},\ Fe^{+++}}} + E^0_{\mathrm{I^-;\ I_2,\ Pt}} = -0.771 + (+0.535) = -0.236$$

$$\Delta F^0 = -nFE^0 = -\left(-1 \times \frac{96{,}500}{4.1840} \times 0.236\right) = 5445\ \mathrm{cal}$$

The positive value of ΔF^0 (or negative value of E^0) indicates that the reaction will not go spontaneously; that is, solid iodine will not react with ferrous ion at unit activity to produce ferric ion at unit activity and iodide ion at unit activity.

However, if the reaction is written in the opposite direction $\mathrm{Fe^{+++}} + \mathrm{I^-} = \mathrm{Fe^{++}} + \tfrac{1}{2}\mathrm{I_2}(s)$, and the oxidation reaction $\mathrm{I^-} = \tfrac{1}{2}\mathrm{I_2} + e$ placed at the left, the cell is written

$$\mathrm{Pt,\ I_2}\ (s);\ \mathrm{I^-}\ (a = 1) \parallel \mathrm{Fe^{++}},\ \mathrm{Fe^{+++}}\ (a = 1);\ \mathrm{Pt}$$

Then,

$$E^0 = E_{\mathrm{Pt,\ I_2;\ I^-}} + E^0_{\mathrm{Fe^{++},\ Fe^{+++};\ Pt}} = -0.535 + (+0.771) = 0.236$$

and

$$\Delta F^0 = -nFE^0 = -1 \times \frac{96{,}500}{4.1840} \times 0.236 = -5445\ \mathrm{cal}$$

The negative value of ΔF^0 (or the positive value of E^0) signifies that the reaction as written is spontaneous; that is, iodide ion will reduce ferric ion to ferrous ion or ferric ion will oxidize the iodide ion to iodine.

This reaction illustrates *convention 4*, according to which for any electrode the atom or ion in the lowest state of oxidation (with the most electrons) will reduce the oxidized form of any atom or ion which has a position lower in the table of standard electrode potentials (all ions being at unit activity).

Chemical Equilibria and Electromotive Force. It was shown on page 269 that, in a reaction,

$$aA + bB = gG + hH$$

$$\Delta F = -RT \ln \frac{a_G{}^g \times a_H{}^h}{a_A{}^a \times a_B{}^b} + RT \ln \frac{a'_G{}^g \times a'_H{}^h}{a'_A{}^a \times a'_B{}^b}$$

$$= -RT \ln K + RT \ln Q \qquad (5)$$

where K represents the equilibrium constant involving the effective concentrations in a state of equilibrium, and Q represents the activity quotient, that is, the ratio of the activities of the products to the activities of the reactants at any specified activities.

Remembering that according to equation 1

$$\Delta F = -nFE$$

and substituting equation 1 into equation 5, we have

$$E = \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln Q \qquad (6)$$

When the reaction is so planned that the reactants start at unit activity, and the final products are produced in concentrations such that their activities are unity, then ΔF is written ΔF^0 and the last term becomes zero. Then equation 5 becomes

$$\Delta F^0 = -RT \ln K$$

Also, in this special case where all the reactants and products are at unit activity, E is defined as E^0. Then,

$$E^0 = \frac{RT}{nF} \ln K \qquad (7)$$

Substituting equation 7 into equation 6 gives

$$E = E^0 - \frac{RT}{nF} \ln \frac{a'_G{}^g \times a'_H{}^h}{a'_A{}^a \times a'_B{}^b} = E^0 - \frac{RT}{nF} \ln Q$$

$$= E^0 - \frac{8.314 \times T \times 2.303}{n \times 96{,}500} \log Q \qquad (8)$$

When $T = 298.1$ and $n = 1$

$$E = E^0 - 0.0591 \log Q \qquad (9)$$

These equations are extremely important in the study of electrochemistry. Many special formulas concerned with theoretical and practical applications of electromotive-force measurements follow directly from them. Equation 7 is used for calculations involving systems at equilibrium, and the more general equation 8 is used for systems which are not in a state of equilibrium.

Example 6. Calculate from electromotive-force data the equilibrium constant for the reaction between tin and lead and their ions at unit activity, thus:

$$Sn + Pb^{++} = Pb + Sn^{++}$$

Splitting up the reaction into the two electrode reactions,

$$Sn = Sn^{++} + 2e \quad \text{and} \quad Pb^{++} + 2e = Pb$$

and putting the oxidation reaction at the left in the corresponding cell at 25°, we have

$$Sn;\ Sn^{++}\ (a = 1) \parallel Pb^{++}\ (a = 1);\ Pb$$

$$E^0 = E^0_{Sn;\ Sn^{++}} + E^0_{Pb^{++};\ Pb} = 0.140 + (-0.126) = 0.014 \text{ volt}$$

$$E^0 = 0.014 \quad \text{and} \quad \Delta F^0 = -nFE^0 = -643 \text{ cal}$$

$$E^0 = \frac{RT}{nF} \ln K = \frac{8.314 \times 298.1 \times 2.303}{2 \times 96{,}500} \log K = 0.0296 \log K$$

$$K = \frac{a_{Sn^{++}}}{a_{Pb^{++}}} = 2.97$$

In other words, when tin is added to a solution of lead salt, a state of equilibrium is reached in which the activity of the tin ions is 2.97 times as great as that of lead ions.

In checking this equilibrium Noyes and Toabe added metallic tin to a solution of lead perchlorate at 25° and found at equilibrium 0.0716 mole of tin perchlorate and 0.0242 mole of lead perchlorate per liter. If we assume that the concen-

trations of tin perchlorate and lead perchlorate may be used in place of the activities,*

$$K = \frac{a_{Sn^{++}}}{a_{Pb^{++}}} = \frac{0.0716}{0.0242} = 2.96$$

In order to approach the equilibrium from both sides they also added lead to a solution of tin perchlorate and found at equilibrium 0.0704 mole of tin perchlorate and 0.0233 mole of lead perchlorate per liter.

$$K = \frac{a_{Sn^{++}}}{a_{Pb^{++}}} = \frac{0.0704}{0.0233} = 3.02$$

Carrying out a similar calculation for the addition of zinc to copper ions, we find that $E^0 = 1.1071$ and $K = \frac{a_{Zn^{++}}}{a_{Cu^{++}}} = 10^{37}$. In other words, the removal of copper ions by zinc is practically complete.

With reference to Table III any electrolyte in the reduced or "ous" state (at unit activity) will tend to reduce any electrolyte in the oxidized or "ic" state (at unit activity) which is lower in the table. Any combination of electrodes may be made, and from the corresponding voltage the equilibrium constant may be calculated.

Example 7. To what extent will mercuric ion be reduced by the addition of ferrous ion at 25°?

The cell is

$$Pt;\ Fe^{++}\ (a = 1),\ Fe^{+++}\ (a = 1)\ \|\ Hg^{++}\ (a = 1),\ Hg_2^{++}\ (a = 1);\ Pt$$

$$E^0 = E^0_{Pt(Fe^{++},\ Fe^{+++})} + E^0_{(Hg^{++},\ Hg_2^{++})Pt}$$

$$= -0.771 + 0.910 = 0.139$$

The cell reaction is

$$Fe^{++} + Hg^{++} = Fe^{+++} + \tfrac{1}{2}Hg_2^{++}$$

$$E^0 = 0.139 = \frac{8.314 \times 298.1 \times 2.303}{1 \times 96{,}500} \log K$$

$$K = \frac{a_{Fe^{+++}} \times a_{Hg_2^{++}}{}^{1/2}}{a_{Fe^{++}} \times a_{Hg^{++}}} = \text{antilog } 2.350 = 224$$

This calculation shows that the ferrous ion reduces the mercuric ion to such an extent that, at equilibrium, the product of the activity of the ferric ion by the square root of the activity of the mercurous ion (Hg_2^{++}) is 224 times as great as the product of the activities of the ferrous and mercuric ions.

* This assumption is not safe except in very dilute solutions. The error involved is reduced in cases of this kind where all the ions have the same valence and the correction factors tend to cancel out.

These examples have served to illustrate equation 7 which gives the relation between the equilibrium constant and the standard electrode potentials. The more general equation 8 which shows the relation among E, E^0, and Q will now be applied. It can be used to calculate the voltage of a cell when the ions are not at unit activity and to calculate the activity of ions from a measurement of the electromotive force of the cell.

Example 8. Calculate the potential of the following cell at 25°.

$$\mathrm{Sn};\ \mathrm{Sn^{++}}\ (a = 0.6)\ \|\ \mathrm{Pb^{++}}\ (a = 0.3);\ \mathrm{Pb}$$

which is similar to that shown in example 6. The cell reaction is

$$\mathrm{Sn} + \mathrm{Pb^{++}} = \mathrm{Sn^{++}} + \mathrm{Pb}$$

$$E = E^0 - \frac{RT}{nF} \ln Q = E^0 - \frac{RT}{nF} \ln \frac{a_{\mathrm{Sn^{++}}}}{a_{\mathrm{Pb^{++}}}}$$

$$= 0.0140 - \frac{0.0591}{2} \log \frac{0.6}{0.3}$$

$$= 0.0140 - 0.0089 = 0.0051 \text{ volt}$$

$$\Delta F = -EnF = -2 \times \frac{96{,}500}{4.1840} \times 0.0051 = -235 \text{ cal}$$

The free energy decrease ΔF for this reaction is less than ΔF^0 for the reaction where both reactants and products are at unit activity (example 6), because here the specified activity of the products is greater than the specified activity of the reactants. The activities 0.3 and 0.6 are arbitrarily assigned and are not to be confused with the equilibrium concentrations.

The validity of equation 8 may be illustrated by determining the potential of the ferric–ferrous electrode using the cell,

$$\mathrm{Pt},\ \mathrm{H_2}\ (1 \text{ atm});\ \mathrm{H^+}\ (a = 1)\ \|\ \mathrm{Fe^{++}}\ (a = x),\ \mathrm{Fe^{+++}}\ (a = y);\ \mathrm{Pt}$$

The cell reaction is

$$\tfrac{1}{2}\mathrm{H_2} + \mathrm{Fe^{+++}} = \mathrm{Fe^{++}} + \mathrm{H^+}$$

Applying equation 8

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{\mathrm{H^+}} \times a_{\mathrm{Fe^{++}}}}{a_{\mathrm{H_2}}^{1/2} \times a_{\mathrm{Fe^{+++}}}}$$

but, since $a_{\mathrm{H^+}} = 1$ and $a_{\mathrm{H_2}} = 1$,

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{\mathrm{Fe^{++}}}}{a_{\mathrm{Fe^{+++}}}} \tag{10}$$

E^0 is the electromotive force of an inert electrode surrounded by equal activities of ferrous and ferric ions when measured against the standard

hydrogen electrode, for, when $a_{Fe^{++}}$ and $a_{Fe^{+++}}$ are equal, the last term becomes zero.

E^0, as calculated from the data E of Peters,* shown in Table IV, is reasonably constant even though the ratios are the ratios of concentrations rather than activities.

TABLE IV

Change of Voltage with Change in Ratio of Oxidizing to Reducing Ions

$c_{Fe^{+++}}/c_{Fe^{++}}$	0.5/99.5	2/98	10/90	30/70	50/50	80/20
$-E$	0.580	0.615	0.655	0.690	0.713	0.747
$-E^0$	0.712	0.712	0.710	0.711	0.713	0.712

The absolute values of E^0 are only approximate, because no attempt was made to obtain activities. The solutions were made tenth-normal with respect to hydrochloric acid to prevent hydrolysis.

Popoff and Kunz have investigated this system more fully, extrapolating to zero concentration of iron ions and zero concentration of hydrochloric acid. They obtained a series of values of E^0 in progressively more dilute solutions of ferrous and ferric chloride and extrapolated to infinite dilution of iron chlorides. This extrapolated value of E^0 in $N/10$ hydrochloric acid is -0.731, an accurate value obtained with activities instead of concentrations. There is a complication, however, in that the hydrochloric acid changes the character of the solution and affects the value of E^0. A value of -0.747 for E^0 in pure water was obtained by determining the extrapolated value of E^0 in solutions of different normality with respect to hydrochloric acid and extrapolating these values to zero concentration of hydrochloric acid. The value is somewhat in doubt on account of hydrolysis. Schumb and Sweetzer † obtained a value of -0.783 by measuring the equilibrium between silver and ferric perchlorate. The value selected by Latimer is -0.771.

Concentration Cells. When two electrodes of the same material are immersed in solutions of their ions at the same concentration, there will be no difference of potential. If, however, the two solutions are of different concentrations, the cell will exhibit a definite electromotive force which depends on the ratio of the activities of the ions in the two solutions. Such a cell is represented by the arrangement

$$M;\ M^+(a_1)\ ||\ M^+(a_2);\ M$$

* Peters, *Z. physik. Chem.*, **26**, 193 (1898).

† Schumb and Sweetzer, *J. Am. Chem. Soc.*, **57**, 871 (1935).

Writing the cell reaction in such a way that the left electrode is oxidized and the electrode at the right is reduced, we have

$$\begin{aligned} M &= M^+(a_1) + e \\ M^+(a_2) + e &= M \end{aligned} \qquad (11)$$

$$M^+(a_2) = M^+(a_1)$$

The mathematical formulation of this cell is particularly simple because the reactants and the products are the same. Referring to the fundamental formula 8, placing the products in the numerator as usual, neglecting solids because the activities of solids are taken as unity, and considering only the activities of the M^+ ion, we find

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_1}{a_2}$$

But $E^0 = \frac{RT}{nF} \ln K$, and for this case $K = 1$ because equilibrium is established only when $a_1 = a_2$.

Then $E^0 = 0$, and

$$E = -\frac{RT}{nF} \ln \frac{a_1}{a_2} \qquad (12)$$

If, for example, the concentrations of the univalent metal ions are such that $a_1 = 0.01$ and $a_2 = 0.1$, the electromotive force is given by the relation,

$$E = -\frac{8.314 \times 298.1 \times 2.303}{96{,}500} \log \frac{0.01}{0.1} = 0.0591 \text{ volt}$$

The positive value of E shows that the reaction is spontaneous; that is, there is a tendency for ions at $a_2 = 0.1$ to diffuse into the more dilute solutions where $a_1 = 0.01$. The electrode, immersed in the solution of positive ions where $a_2 = 0.1$ is positive with reference to the more dilute solution, because there are more collisions of positive ions per second per square centimeter on the surface of the electrode. Inasmuch as this positive electrode is placed at the right, the electrode at the left is negative with respect to it, and the electromotive force of the cell has a positive value in agreement with convention and in agreement with the calculations of equation 12.

Example 9. If the more concentrated solution of activity 0.1 had been placed at the left instead of the right, the negative electrode would have been at the right, and, according to convention, the electromotive force of the galvanic cell

would have had a negative value. This convention is in agreement with the calculations just developed.

$$E = -\frac{8.314 \times 298.1 \times 2.303}{96{,}500} \log \frac{0.1}{0.01} = -0.0591$$

The cell reaction $M^+ (a_2 = 0.01) = M^+ (a_1 = 0.1)$ is not spontaneous.

In dilute solutions, where the activities are nearly the same as the concentrations, equation 13 may be used as an approximate form of equation 12 for positive ions where c_1 is the concentration at the left electrode and c_2 is the concentration at the right.

$$E = -\frac{RT}{nF} \ln \frac{c_1}{c_2} \tag{13}$$

If the cell is made with negative ions M^-, such as iodide ions, the arrangement is

$$M; M^-(a_1) \,||\, M^-(a_2); M$$

The cell reaction is

Left electrode	$M^-(a_1) = M + e$	(oxidation)
Right electrode	$M + e = M^-(a_2)$	(reduction)
	$M^-(a_1) = M^-(a_2)$	

and the formula for the voltage of the concentration cell with negative ions is

$$E = -\frac{RT}{nF} \ln \frac{a_2}{a_1} \cong -\frac{RT}{nF} \ln \frac{c_2}{c_1} \tag{14}$$

In another type of concentration cell the activity of ions in solution is uniform throughout the cell, but the concentration of the material in the two electrodes is different. For example, if two hydrogen electrodes at different pressures of hydrogen are placed in a solution of hydrogen ions, the electrode which has hydrogen at the greater pressure will tend to produce more hydrogen ions and, thus, make the electrode negative with respect to the other. The electromotive force of the cell can be calculated from the partial pressures. Thus:

$$\mathrm{Pt}, \mathrm{H_2}(p_1); \mathrm{H^+}; \mathrm{H_2}(p_2), \mathrm{Pt}$$

The cell reaction is

$$\mathrm{H_2}(p_1) = \mathrm{H_2}(p_2)$$

and

$$E = -\frac{RT}{nF} \ln \frac{p_{\mathrm{H_2},2}}{p_{\mathrm{H_2},1}}$$

Example 10. Two hydrogen electrodes are set in a solution of hydrochloric acid at 25°. The pressure of hydrogen over one is 1 atm, and over the other it is 0.5 atm. This reduction in partial pressure of hydrogen is accomplished by mixing the hydrogen with helium or nitrogen or other inert gas. What is the electromotive force of the cell?

If the electrode at 1 atm is placed at the left $p_1 = 1$ and

$$E = -\frac{RT}{nF}\ln\frac{p_2}{p_1} = -\frac{0.0591}{2}\log\frac{0.5}{1} = 0.0089 \text{ volt}$$

The Hydrogen Electrode. The experimental determination of the activity of hydrogen ions in a solution is of great practical importance, and the hydrogen electrode was the first means of making these determinations. It still remains the standard of reference, although more rapid and convenient electrodes are now available for many routine measurements.

Hydrogen gas does not conduct the electric current, and it cannot be used alone as an electrode, but, when adsorbed on the surface of platinum, it behaves just as if it were a metallic electrode, and the reaction,

$$\tfrac{1}{2}H_2 = H^+ + e$$

is completely reversible, as shown by laboratory tests and by thermodynamic criteria. Hydrogen ions apparently can break away from the layer of hydrogen atoms adsorbed on the surface; and the platinum acts as an inert electric conductor without entering the reaction of the cell. To act efficiently, the electrode must be covered with platinum black to give a large surface area for adsorption. The electrode is arranged in such a way that hydrogen bubbles up around the platinum, or else the electrode is immersed partly in the solution and partly in the hydrogen. The level of the liquid is changed as the gas bubbles out from a glass hood which surrounds the electrode, and, thus, the electrode is bathed alternately with hydrogen and with the solution.

Numerous forms of hydrogen electrodes have been devised but the general form already shown in Fig. 110 is satisfactory. In accurate work the hydrogen must be at a definite known pressure, and it must contain no oxygen. Corrections may be made for the vapor pressure of water. Several solutes may interfere with the proper operation of the hydrogen electrode, particularly oxidizing agents or platinum poisons.

Any oxidizing substances such as ferric or nitrate ions or chromates or unsaturated organic compounds which can be reduced by hydrogen in the presence of platinum must be avoided. Traces of arsenic and sulfur compounds may react with active platinum atoms at the surface

thus diminishing the adsorptive properties for hydrogen and giving erroneous potentials.

In some solutions it is not feasible to bubble hydrogen through the cell because the solution is in equilibrium with other gases which would be swept out by the hydrogen. For example, in determining the hydrogen ion activity in blood, hydrogen is shaken in a closed cell with the platinized platinum electrode. If hydrogen is swept through the cell, it will remove carbon dioxide with a consequent change in the hydrogen ion concentration.

The determination of hydrogen-ion activity with the hydrogen electrode is merely an application of formula 12 for the electromotive force of a concentration cell, set up in principle as follows:

$$\mathrm{Pt,\ H_2}\ (p = 1);\ \mathrm{H^+}(a)\ ||\ \mathrm{H^+}\ (a = 1);\ \mathrm{H_2}\ (p = 1),\ \mathrm{Pt}$$

One of the two hydrogen electrodes under a hydrogen pressure of 1 atm is placed in a solution of H^+ ions having an activity of 1, and the other hydrogen electrode is placed in a solution in which it is desired to measure the activity of hydrogen ion. The two solutions are connected by a salt bridge, and the electromotive force of the cell is measured with a potentiometer.

The cell reaction is

$$\begin{aligned} &\tfrac{1}{2}\mathrm{H_2} = \mathrm{H^+}(a) + e \qquad \text{(oxidation at the left)} \\ &e + \mathrm{H^+}(a = 1) = \tfrac{1}{2}\mathrm{H_2} \qquad \text{(reduction at the right)} \\ &\overline{\mathrm{H^+}(a = 1) = \mathrm{H^+}(a)} \end{aligned}$$

and, applying equation 12, we have

$$E = -\frac{RT}{nF}\ln\frac{a_{\mathrm{H^+}}}{1} = -\frac{RT}{nF}\ln a_{\mathrm{H^+}} \tag{15}$$

In practice it is much easier to use a normal calomel cell in place of a standard hydrogen electrode. Careful measurements have shown that the normal calomel electrode with a normal KCl bridge is negative with respect to the standard hydrogen electrode by 0.2802 volt at 25°.

The formula for the hydrogen electrode at 1 atm pressure against a normal calomel electrode with a normal KCl bridge at 25° is

$$E - 0.2802 = -0.0591 \log a_{\mathrm{H^+}} \tag{16}$$

Although this formula applies strictly only to activities of hydrogen ions, it can be used with fair approximation in dilute solutions for the concentrations of hydrogen ions.

There is an uncertainty regarding the junction potential which prevents the accurate determination of absolute values of individual ion activities. No matter what the theoretical background is, the practical value of the hydrogen electrode has been abundantly established. The voltage measurements obtained from hydrogen electrodes are correlated, quantitatively, with a wide variety of chemical and biological phenomena.

The fundamental difference between hydrogen-ion activity as registered by a hydrogen electrode, and the number of milliliters of alkali which are needed to neutralize the acid, must be clearly understood. The latter corresponds to a "reserve" acidity, that is, to ionized and un-ionized acid, but the former gives the actual conditions of acidity, that is, hydrogen-ion activity.

***p*H.** Hydrogen-ion activities are determined down to very low values, and in order to avoid the nuisance of writing one to a dozen and more zeros to describe them, it has been found useful to use an exponential notation. The term *p*H first proposed in 1909 by Sorensen is widely used. It is defined as the negative exponent of 10 which gives the hydrogen-ion activity.

Thus,

$$10^{-pH} = a_{H^+}$$

or

$$pH = -\log a_{H^+} = \log \frac{1}{a_{H^+}} \tag{17}$$

Example 11. What is the activity of hydrogen ions in a solution which has a *p*H of 4?

$$a_{H^+} = 10^{-pH} = 10^{-4} = 0.0001$$

What is the *p*H of a solution in which the activity of H^+ is 0.0002?

$$pH = \log \frac{1}{a_{H^+}} = \log \frac{1}{2 \times 10^{-4}} = \log 5 \times 10^3 = 3.699 \text{ *}$$

Equation 16 for the hydrogen electrode at 1 atm pressure and the normal calomel electrode can be converted into equation 18.

$$E - 0.2802 = -0.0591 \log a_{H^+} = 0.0591\ pH$$

or

$$pH = \frac{E - 0.2802}{0.0591} \tag{18}$$

* The calculation may also be made as follows: $pH = -\log a_{H^+} = -\log (2 \times 10^{-4}) = -(4 + 0.301) = 3.699$. Further examples of negative logarithms of this type are given in Daniels, "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., New York, 1928, page 11.

It is shown on page 490 that the product of the hydrogen and hydroxyl ions at 25° in any solution is always

$$a_{H^+} \times a_{OH^-} = 1 \times 10^{-14}$$

Thus, if a solution contains exactly as many hydroxyl ions as hydrogen ions, the solution is neutral, and $a_{H^+} = a_{OH^-} = 10^{-7}$. The pH of a neutral solution then is 7. Addition of an acid increases the value of a_{H^+} and gives a pH less than 7. Addition of a base with its extra OH^- ions reduces the value of a_{H^+} and increases the pH above 7.

Example 12. What is the activity of hydrogen ions and the pH of a solution which has an activity of hydroxyl ions a_{OH^-} of 0.001?

$$a_{H^+} = \frac{1 \times 10^{-14}}{a_{OH^-}} = \frac{1 \times 10^{-14}}{10^{-3}} = 1 \times 10^{-11}$$

$$p\text{H} = -\log a_{H^+} = -\log 10^{-11} = 11$$

Table V gives the activities of hydrogen ions and the pH of typical solutions.

TABLE V

ACTIVITIES AND pH OF TYPICAL ACIDS AND BASES

Solute	*Moles per liter*	a_{H^+}	pH
Hydrochloric acid	1.0	8.0×10^{-1}	0.1
	0.1	8.5×10^{-2}	1.07
	0.01	9.6×10^{-3}	2.02
	0.001	9.7×10^{-4}	3.01
Sulfuric acid	0.05	5.9×10^{-2}	1.23
Acetic acid	1.0	4.3×10^{-3}	2.37
	0.1	1.3×10^{-3}	2.87
	0.01	4.3×10^{-4}	3.37
Ammonium hydroxide	1.0	1.7×10^{-12}	11.77
	0.1	5.4×10^{-12}	11.27
	0.01	1.7×10^{-11}	10.77
Sodium hydroxide	1.0	8.9×10^{-15}	14.05
	0.1	8.5×10^{-14}	13.07
	0.01	7.6×10^{-13}	12.12

Other Electrodes for Measuring Hydrogen-Ion Activities. The practical limitations of the hydrogen electrode in certain solutions has been discussed. A wide selection of colorimetric indicators is available which change color at definite pH's. They are used extensively in analytical work, but they are limited to transparent solutions, and, as a rule, they are less accurate indicators of pH than the electrometric methods. Theoretically, any reaction involving hydrogen ions or hydroxyl ions

can be used, provided a suitable reversible electrode is available. The three most important electrodes used for measuring hydrogen–ion activity are described here briefly.

The Quinhydrone Electrode. When a little quinhydrone is dissolved in a solution and a platinum or gold or other inert electrode is introduced, the potential of this electrode may be used to determine the activity of hydrogen ions in the solution. A molecule of quinhydrone contains one molecule of quinone ($C_6H_4O_2$) and one of hydroquinone [$C_6H_4(OH)_2$] held together in a loose compound. Hydroquinone is a weak acid dissociating slightly according to the reaction,

$$C_6H_4(OH)_2 = C_6H_4O_2^{--} + 2H^+$$

Quinone may be reduced to hydroquinone *ion* by the addition of two electrons according to the reaction,

$$C_6H_4O_2 + 2e = C_6H_4O_2^{--}$$

Then the hydroquinone ion combines with hydrogen ions to give hydroquinone, according to the reverse of the first reaction. The whole reaction is

$$2H^+ + \underset{\text{Quinone}}{C_6H_4O_2} + 2e \rightleftharpoons \underset{\text{Hydroquinone}}{C_6H_4(OH)_2}$$

Substituting into equation 8, we find that the quantitative relation is

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{\text{hydroquinone}}}{a_{H^+}{}^2 \times a_{\text{quinone}}}$$

Since the concentrations of quinone and hydroquinone are equal, because the quinhydrone added contains an equal number of moles of each, the ratio of their activities is nearly unity, and we have at 25°

$$E = E_1{}^0 + \frac{0.0591}{2} \log a_{H^+}{}^2$$

$$= E_1{}^0 + 0.0591 \log a_{H^+} = E_1{}^0 - 0.0591\ p\text{H} \qquad (19)$$

where $-E_1{}^0$ is the voltage of the quinhydrone electrode against a hydrogen electrode in a solution of unit activity of hydrogen ions. When $a_{H^+} = 1$, experiment shows that E is 0.6996. This, then, is the value of $E_1{}^0$.

When E is referred to the normal calomel electrode,

$$p\text{H} = \frac{0.6996 - 0.2802 - E}{0.0591} = \frac{0.4194 - E}{0.0591} \qquad (20)$$

The quinhydrone electrode is very simple and convenient, and it is not easily poisoned. It cannot be used in strongly alkaline solutions on account of the oxidation by air of the hydroquinone above a pH of 8, and it may give inaccurate results in concentrated salt solutions, because the activity of the quinone and hydroquinone may be affected differently, and, thus, although the ratio $\frac{c_{\text{hydroquinone}}}{c_{\text{quinone}}}$ is unity, the ratio $\frac{a_{\text{hydroquinone}}}{a_{\text{quinone}}}$ may not be unity. This salt error can be neglected in ordinary dilute solutions.

Oxide Electrodes. Certain metallic oxides of low solubility may be used as hydrogen-ion indicators. For example, with a divalent metal the electrode reaction is,

$$MO + 2H^+ + 2e = M + H_2O$$

and

$$E_1 = E_1^0 + 0.0591 \log a_{H^+} \qquad (21)$$

The constant E_1^0 is evaluated experimentally from solutions of known hydrogen-ion activity using the hydrogen electrode or other reference electrode. The antimony oxide electrode against the hydrogen electrode is used with the formula,

$$E_1 = E_1^0 + 0.0591 \log a_{H^+} = 0.144 - 0.0591\ p\text{H}$$

between pH 5 and 10 when air is excluded and precautions are taken to have the stable cubic form of the oxide.*

The Glass Electrode. A very thin membrane of glass separating two solutions gives potentials which depend directly on the hydrogen-ion concentrations. The resistance of the glass diaphragm is so great that an electron-tube voltmeter is used to measure the voltages. The membrane is mounted in a cell of the following type:

Calomel electrode || solution of known pH; glass membrane; solution of unknown pH || calomel electrode

The voltage is a logarithmic function of the difference in hydrogen-ion activity except for a small "asymmetry potential" due to the glass. This may be evaluated by using solutions of known pH on each side of the membrane. The glass electrode is not affected by oxidizing solutions, and it can be used in nonaqueous solutions and frequently where the hydrogen electrode cannot be used. This electrode is not suitable for use in strongly alkaline solutions. Improvements in the composition

* Roberts and Fenwick, *J. Am. Chem. Soc.*, **50**, 2125 (1928).

of glass suitable for electrodes together with greater sensitivity to small currents have made possible the use of less fragile glass membranes, and the electron tubes and circuits have been perfected to such a point that the glass electrode is tending to displace other electrodes for the determination of *p*H in industrial operations. It finds wide application in control, in biological investigations, and in analytical chemistry.

The mechanism by which the thin glass membrane responds to the hydrogen-ion activity is not thoroughly understood, but it probably involves an adsorption of hydrogen ions on both sides of the membrane, which is in each case proportional to the activity of the hydrogen ions in the solutions. The theory and use of the glass electrode have been fully treated by Dole.*

Electrodes suitable for determining the activity of hydrogen ions have reached a high state of perfection; activities of copper, silver, zinc, and other ions can also be determined with a high degree of precision using metallic electrodes.

There is a need for electrodes capable of measuring ion activities of calcium, sodium, and potassium as distinguished from the concentration of the salts. When the metals of these elements are dissolved in mercury in dilute solution and allowed to drop from a fine capillary, fair results can be obtained in certain solutions. A fresh surface of the amalgam is exposed continuously so that there is not time to change the concentration of metal and effect the electrode potential. These electrodes have not been satisfactory, however, with blood and other biological solutions containing proteins where they would be particularly useful.

Chlorine may be used with a platinum electrode as a gas electrode for determining the activity of chloride ions in the same way that the hydrogen electrode is used for determining hydrogen ions but only a few other gases can be used as reversible electrodes.

Potentiometric Titrations. When one solution is added to another from a buret, as, for example, in the titration of a base with an acid, it is possible not only to determine the end point with great accuracy but also to know the activity of the hydrogen ion during the course of the titration. The hydrogen electrode or other hydrogen-ion-indicating electrode and a calomel electrode are placed directly in the solution, as shown in Fig. 110, and the electromotive force is observed at frequent intervals during the titration.

Figure 112 gives the electromotive force of the hydrogen electrode against the standard hydrogen electrode, plotted against the gram equivalents of NaOH added to a gram equivalent of a strong acid and two

* Dole, "The Glass Electrode," John Wiley & Sons, New York, 1941.

weak acids. The hydrogen activities and pH values, as calculated from equations 16 and 18, are plotted vertically at the right.

We will consider first the titration of hydrochloric acid with sodium hydroxide, shown in the lowermost curve. When the solution is exactly

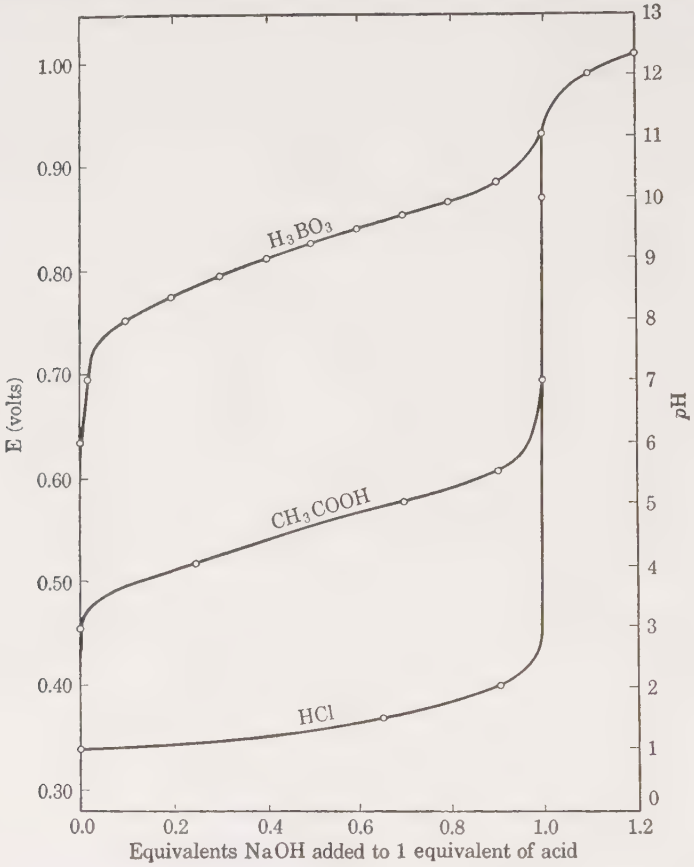


FIG. 112. Electromotive force of hydrogen electrode in the titration of strong and weak acids by sodium hydroxide.

neutral, the activities of the hydrogen ions and hydroxyl ions are the same and equal to 10^{-7} at 25°. The voltage of the hydrogen electrode against the calomel electrode, then, is

$$E = 0.0591 \log \frac{1}{1 \times 10^{-7}} + 0.2802 = 0.6942 \text{ volt}$$

At the end point the concentration of hydrogen ions is very small, and the number of hydrogen ions in a drop of acid, or of hydroxyl ions

in a drop of alkali, is large in comparison. A slight addition of either acid or alkali then makes a large change in the hydrogen-ion activity. If we regard the solutions before and after the addition of alkali as the two solutions of a concentration cell, it is seen that the voltage change must be large when the ratio a_1/a_2 of equation 12 is large. Near the end point, then, a milliliter will give a much greater change in voltage and a steeper curve. When the solution is already strongly acid or strongly alkaline, the addition of a few more hydrogen or hydroxyl ions from a buret has only a slight effect, and the curve is flat.

Acetic acid shown in the middle curve of Fig. 112 gives an initial electromotive force greater than that of hydrochloric acid, because it is slightly dissociated, and the hydrogen-ion concentration at a given concentration of acid is much less. It should be noticed that the first additions of alkali cause a marked decrease in acidity. The alkali not only neutralizes the acid and thereby converts hydrogen ions into water but also produces sodium acetate which is largely dissociated. The large increase in acetate ions causes the repression of ionization of the acetic acid and, in turn, causes more hydrogen ions to change into undissociated acetic acid molecules (page 488).

The upper curve is for boric acid, an acid which is still weaker than acetic acid. Addition of OH^- ions causes the acidity to decrease slowly until the neutral point is reached, when a sudden change takes place.

It can be shown that the middle of this steep part of the curve corresponds to the normal salt, where both acid and base are present in exactly equivalent amounts. For sodium hydroxide and hydrochloric acid this end point comes at the neutral point where $p\mathrm{H} = 7$. When weak acids or bases are used, the end point corresponding to equivalent amounts of acid and base will not come at a pH of 7, because the salts produced by the neutralization are hydrolyzed, as explained later on page 496.

Figure 113 shows how the activity of hydrogen ion increases as hydrochloric acid is added to sodium carbonate which gives one end point corresponding to the formation of bicarbonate ion and another corresponding to the formation of carbonic acid.

The first is represented by the equilibrium,

$$CO_3^{--} + H^+ = HCO_3^-$$

and the second by the equilibrium,

$$HCO_3^- + H^+ = H_2CO_3$$

It was known empirically, long before these titration curves were available, that phenolphthalein is a suitable indicator for the carbonate and

methyl orange for the bicarbonate. The former changes color at a *p*H of about 9 and the latter at about 4, corresponding to the steep parts of the curve, and the reason for this choice of indicators is now evident.

For many purposes it is necessary to know only the end point in the titration, and it is not necessary to know the actual activities of the

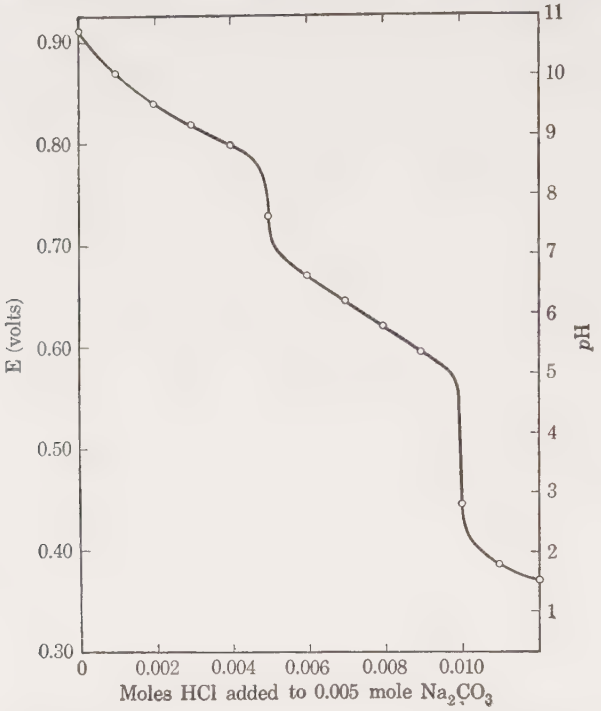


Fig. 113. Electromotive force of hydrogen electrode in the titration of polyacidic base with hydrochloric acid.

ions. The problem is then simpler, and it is not necessary to have reversible electrodes nor to use the absolute values of the electromotive force in calculations. A reagent is added gradually until the voltage changes rapidly with the addition of a slight amount of reagent. Sometimes the voltage change is so great as to be noted directly on a galvanometer, but more often the voltages E are plotted against the volume V of reagent added, and the steepest part of the curve is located by inspection. Examples of neutralizations were given in Figs. 112 and 113. When oxidation–reductions are involved, it is sufficient to insert a platinum wire in the solution and connect it to a calomel electrode through a galvanometer, a balanced voltmeter as shown in Fig. 110, or a potentiometer as shown in Fig. 111.

Sometimes the point of inflection in the curve is not sufficiently pronounced to determine accurately, and then it is helpful to plot tangents of the curve $\Delta E/\Delta V$ against the volume V of reagent added, as shown in **Fig. 114.** The sharp peak in this curve gives the end point with certainty. The differential graph may be obtained by drawing tangents at

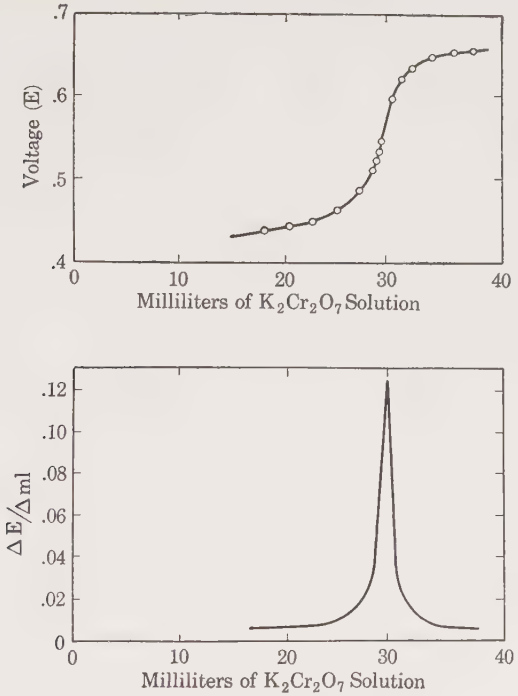


FIG. 114. Potentiometric titration of ferrous sulfate with potassium dichromate showing method of tangents.

points on the voltage curve, or it may be obtained directly from the original data by dividing the differences in voltage by the corresponding differences in milliliters.

For determining end points in neutralizations it is possible to bubble oxygen or even air over a platinized platinum electrode. Since the oxygen electrode is not reversible, it is not possible to set nFE equal to ΔF, and no theoretical significance can be attached to the absolute voltages. But when addition of reagent leads to a rapid change of OH^- ions and of potential the end point can be identified.

In addition to neutralizations and oxidations, it is possible to obtain end points in precipitations. The titration of iodide with silver nitrate is a simple example. A silver wire is placed in the solution and con-

nected to a calomel reference electrode through a galvanometer which is set at zero by opposing a potential from a battery and adjustable rheostat. As the silver solution is added, the galvanometer remains near zero because the silver-ion concentration is fixed by the solubility of silver iodide. When all the iodide is precipitated, however, the next drop increases the silver-ion concentration enormously and the galvanometer is deflected sharply. An end point with a different electromotive force is obtained for bromides, and, thus, it is possible to determine the amounts of both chlorides and bromides in a mixture of the two.

Junction Potentials. In addition to the potentials at the two electrodes, already discussed, there is a third potential if two different solutions are in contact with each other. If, for example, a concentrated solution of hydrochloric acid touches a dilute solution, both hydrogen ions and chloride ions tend to diffuse from the concentrated solution into the dilute solution. The hydrogen ion moves faster, and, thus, the dilute solution soon becomes positively charged on account of an excess of positive hydrogen ions. The more concentrated solution is left with an excess of negative chloride ions and thus acquires a negative charge. The differential diffusion is soon offset by the charges set up.

In general, it may be stated that the difference of potential set up at the junction of the two solutions is caused by the difference in the rates of migration of the two ions, *the more dilute solution acquiring a charge corresponding to that of the faster-moving ion.*

The difference in potential at the junction of two liquids must be eliminated or corrected in making accurate measurements of electrode potentials. The most convenient way of minimizing this potential is through the use of a salt bridge of potassium chloride connecting the two solutions of different electrolytes.

Potassium chloride is used because the transference numbers of the two ions are about the same, 0.48 for K^+ and 0.52 for Cl^-. Under these conditions each ion moves with nearly the same velocity, and each has the same tendency to give its charge to the more dilute solution.

Other ions than potassium and chloride are usually present at the two ends of the bridge, and it is desirable to minimize the effect of these ions by having a large excess of the potassium chloride. For this purpose saturated potassium chloride is more effective than normal potassium chloride in eliminating the junction potential, but it is more troublesome to use. When potassium chloride cannot be used, as, for example, in a cell containing silver nitrate, a salt bridge of ammonium nitrate is used.

The junction potential E_j may be largely eliminated as just described, or it may be calculated with the help of the following equation,

$$E_j = \frac{v_a - v_c}{v_a + v_c} \frac{RT}{nF} \ln \frac{a_2}{a_1} \tag{22}$$

where a_2 is the activity of the ions in the concentrated solution, a_1 is the activity in the dilute solution, and v_c and v_a are the migration velocities of the cation and anion, respectively. This formula applies to cells with metal electrodes which are reversible with respect to the cation. Its derivation is not given here.

Example 13. Calculate the junction potential when a solution of copper sulfate having $a_{Cu^{++}} = 0.1$ is in contact with a solution having $a_{Cu^{++}} = 0.001$.

$$E_j = \frac{v_a - v_c}{v_a + v_c} \frac{RT}{nF} \ln \frac{a_2}{a_1} = \frac{0.00083 - 0.00036}{0.00083 + 0.00036} \times \frac{0.0591}{2} \log \frac{0.1}{0.001} = 0.0233 \text{ volt}$$

When the concentrations of the two solutions are the same, but only one ion is common to both solutions, the junction potential can be estimated by the following empirical formula: *

$$E_j = \frac{RT}{nF} \ln \frac{\Lambda_2}{\Lambda_1} \tag{23}$$

where Λ_2 and Λ_1 are the equivalent conductances of the two electrolytes.

The evaluation of the junction potential constitutes one of the most difficult problems of electrochemistry. It cannot be calculated with exactness; in fact, its theoretical significance is uncertain, and yet it is useful in trying to give numerical values to the activity of single ions as distinguished from the mean activity of the electrolyte. Such numerical values of the activity of single ions probably have no theoretical significance, but they are useful in many calculations when combined with the activities of other ions.

Particularly in the electrochemistry of nonaqueous solutions, ignorance of junction potentials constitutes a serious handicap. These potentials may be quite large. Nevertheless the uncertainty need not prevent their use in an empirical way for practical measurements, particularly if the measurements involve *differences* in concentration, for then the junction potential is largely canceled out.

Activity of Electrolytes and Ions. The activity of an electrolyte or ion, as previously explained, is used in determining true equilibrium constants. By definition, the activities are equal to the concentrations in very dilute solutions, and the difference between activities and con-

* Lewis and Sargent, *J. Am. Chem. Soc.*, **31**, 363 (1909).

centrations in more concentrated solutions depends on the interaction between all the units in the solution thus making the ions behave differently than they would at infinite dilution.

The simple equations which apply only in dilute solutions may be made applicable also to concentrated solutions by substituting activities, or effective concentrations, for analytically determined concentrations. A similar situation was met with on page 276. This simple artifice is not quite so fundamental as might appear at first sight, for a new and unknown variable, the activity coefficient γ, has been introduced. However, this activity coefficient may be determined experimentally in a number of different ways (in terms of appropriate conventions), and it is a great advantage to be able to use such equations with exactness, even if the evaluation of the new quantity is sometimes rather difficult. Methods for determining activities are given on pages 682 and 686.

From a thermodynamic standpoint and for the purpose of making practical calculations, it is unnecessary to attach physical reality to activities. They can be visualized roughly as effective concentrations but the effective concentrations may vary with the measurement or the purpose of the experiment, whereas the activity is a specific quantity, determined unambiguously by experiment and definition.

The activity of a 1–1 electrolyte may be defined as the product of the ionic activities:

$$a_+ \times a_- = a_{\text{solute}} \tag{24}$$

The activity coefficients γ_+ and γ_- of the ions are defined as the ratios of the activities of the ions to their molal concentrations.

$$\gamma_+ = \frac{a_+}{m}; \qquad \gamma_- = \frac{a_-}{m} \tag{25}$$

By definition, the activity coefficient γ of the electrolyte is

$$\gamma = (\gamma_+ \times \gamma_-)^{1/2} \tag{26}$$

for a 1–1 electrolyte, and, hence, for a 1–1 electrolyte,

$$a_{\text{solute}} = m\gamma_+ \times m\gamma_- = m^2\gamma^2 \tag{27}$$

In dilute solutions it may be considered that the ionic activities are approximately equal

$$a_+ = a_- = m\gamma \tag{28}$$

For other than a 1–1 electrolyte, the expressions are slightly more complicated. Thus, for a salt of the $CaCl_2$ type,

$$a_{CaCl_2} = a_{Ca^{++}} \times a_{Cl^-}{}^2 \tag{29}$$

If the molality of $CaCl_2$ is m, the Ca^{++} concentration is m and the Cl^- concentration $2m$. Therefore

$$\gamma_+ = \frac{a_+}{m}; \qquad \gamma_- = \frac{a_-}{2m} \tag{30}$$

Also,

$$\gamma = (\gamma_+ \times \gamma_-^2)^{1/3} \tag{31}$$

Finally,

$$a_{CaCl_2} = (m\gamma_+)(2m\gamma_-)^2 = 4m^3\gamma^3 \tag{32}$$

The extension to other types of electrolytes is similar.

Cells without Transference. The cells which have been studied thus far have been cells with liquid-junction potentials, called cells *with transference*. Those which do not contain a liquid junction are called cells *without transference*. Through the use of a potassium chloride salt bridge it is possible to reduce greatly the junction potential. Although cells with salt bridges have great practical value, as, for example, in the hydrogen electrode, they are not and probably never will be thermodynamically exact.*

The cells without liquid junctions are free from this difficulty of the junction potential and are thermodynamically exact, except for a small correction for change of transference with concentration, but they are difficult to devise. Moreover, since they are reversible with respect to both ions, the potential of the cell gives the mean activity of both positive and negative ions, and absolute information concerning either one alone is not available. They are used for measuring accurately the mean activities of electrolytes.

Concentration cells may be arranged without liquid junctions by using a metallic conductor between two cells, each having the electrolyte at a different concentration, as shown in the following example:

$$\underset{m_1}{\text{Pt, } H_2\text{; HCl}}\text{; AgCl, Ag, Ag, AgCl; }\underset{m_2}{\text{HCl; } H_2\text{, Pt}} \tag{33}$$

Each of the two cells has a hydrogen electrode and a silver chloride electrode dipping into a solution of HCl at a given concentration. Each electrode is reversible with respect to one of the ions, the hydrogen electrode with respect to hydrogen ion, and the silver chloride electrode with respect to chloride ions. Each of the two ions then gives a concentration cell, and the total electromotive force of the cell must include both.

The electromotive force of the concentration cell given in equation 33 is the sum of the two electromotive forces, as calculated with the help

* Guggenheim, *J. Phys. Chem.*, **34**, 1758 (1930).

of equations 12 and 14 for concentration cells of positive and negative ions as follows:

$$E = E_{H^+} + E_{Cl^-} = -\frac{RT}{nF}\ln\frac{a_{H^+,1}}{a_{H^+,2}} + \frac{RT}{nF}\ln\frac{a_{Cl^-,2}}{a_{Cl^-,1}}$$

$$= -\frac{RT}{nF}\ln\frac{a_{H^+,1}\times a_{Cl^-,1}}{a_{H^+,2}\times a_{Cl^-,2}}$$

In general for any 1–1 electrolyte in which both ions have reversible electrodes, the formula for a concentration cell *without transference* is

$$E = -\frac{RT}{nF}\ln\frac{a_{+,1}\times a_{-,1}}{a_{+,2}\times a_{-,2}}$$

where a_+ and a_- refer to the activities of the positive and negative ions of the electrolyte, and 1 and 2 refer to the different concentrations of the electrolyte, the electrolyte at concentration 1 being placed at the left electrode. Replacing $a_+ \times a_-$ with its equivalent $(m\gamma)^2$ for a 1–1 electrolyte gives

$$E = -\frac{2RT}{nF}\ln\frac{m_1\gamma_1}{m_2\gamma_2} \tag{34}$$

where m_1 and γ_1 refer to the molality and the activity coefficient of the electrolyte at one concentration and m_2 and γ_2 at another. At 25° this formula becomes

$$E = -0.1183\log\frac{m_1\gamma_1}{m_2\gamma_2} \tag{35}$$

This is an important formula which finds extensive use in determining activities and activity coefficients. The concentrations m_1 and m_2 and the electromotive forces are determined experimentally, leaving only γ_1 and γ_2 as unknowns. By extrapolation of E to infinite dilution where $\gamma_1 = 1$, it is possible to determine the activity coefficient and the activities at any concentration. A specific example is worked out in detail for hydrochloric acid in the appendix on page 682. In this general manner, the activity coefficients of the electrolytes given in Table VI have been determined.

It may be noted that the activity coefficients of these electrolytes pass through a distinct minimum value but that the minima do not occur at the same concentration for each solute. In **Fig. 115** the activity coefficients of these typical electrolytes are plotted against the square root of the ionic strength, a term which is defined on page 507.

TABLE VI

ACTIVITY COEFFICIENTS AT 25°

Molality	HCl	KCl	NaCl	NaOH	H_2SO_4	$CaCl_2$	$CdSO_4$
0.005	0.930	0.927	0.928	....	0.643	0.789	.....
0.01	0.906	0.902	0.903	0.89	0.545	0.732	0.476
0.05	0.833	0.817	0.821	0.80	0.341	0.584	0.383
0.10	0.798	0.770	0.778	0.75	0.266	0.524	0.199
0.20	0.768	0.719	0.732	0.71	0.210	0.491	0.137
0.50	0.769	0.652	0.680	0.68	0.155	0.510	0.061
1.00	0.811	0.607	0.656	0.66	0.131	0.725	0.042
2.00	1.011	0.578	0.670	0.68	0.125	1.554	0.030
3.00	1.31	0.574	0.719	....	0.142	3.384	0.026
4.00	1.74	.....	0.791	....	0.172	.....	.....

Usually, the activity coefficients are less than 1, and the activity which may be regarded in an oversimplified way as effective concentrations is less than the analytically determined concentration. Interionic attraction is responsible in large part for this deviation. Sometimes, as in concentrated solutions of hydrochloric acid or calcium chloride, or in nonaqueous solutions, the activity coefficients are found to be much greater than 1. It is of doubtful value to offer a mechanism for activities, but this effective concentration, so much greater than the stoichiometric concentration, may be attributed to a change in the solvent. The activity may be increased by removing solvent quite as well as by increasing the amount of dissolved solute. Calcium chloride, which crystallizes out with water of crystallization, may render some of the water partially inactive as a solvent and thereby make the activity greater in concentrated solutions than the analytically

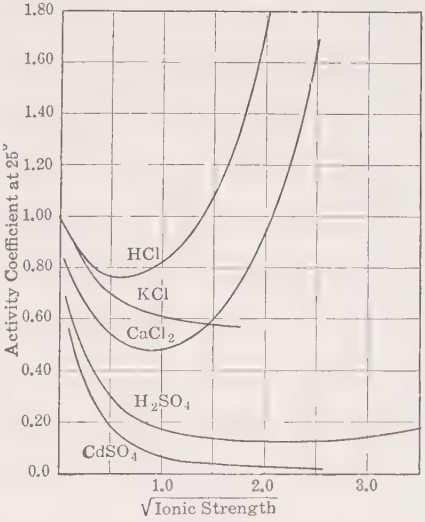


FIG. 115. Activity coefficients of typical electrolytes.

determined concentration. In very concentrated hydrochloric acid solution the high value of the activity coefficient γ probably is due to the presence of hydrochloric acid molecules which are absent in dilute solutions.

The activity coefficients of a large number of electrolytes, both alone and mixed, in solutions of different concentrations have been determined with a high degree of accuracy.* Concentration cells without transference may be made with a connecting wire, as shown in equation 33, or they may be made by using an amalgam in a compartment which is connected with two different solutions, as in the following cell.

$$\underset{m_1}{\text{Ag; AgCl, LiCl; Li(Hg)}_x\text{; LiCl, AgCl; Ag}}\quad\underset{m_2}{}$$

This cell is in reality made up of two independent cells and involves no liquid junction. The molalities of the lithium chloride in the two solutions are m_1 and m_2, and the activity coefficients are γ_1 and γ_2. The electromotive force is given by equation 34, thus:

$$E = -2\frac{RT}{nF}\ln\frac{m_1\gamma_1}{m_2\gamma_2} \tag{36}$$

If two concentration cells are arranged, one, with transference and one without transference, there will be a difference in electromotive force on account of the junction potential. This in turn is determined by the transference number. For example, in the following cell with transference the electrodes of silver chloride are reversible with respect to the chloride ion:

$$\underset{m_1}{\text{Ag; AgCl, LiCl;}}\quad\underset{m_2}{\text{LiCl; AgCl; Ag}}$$

It can be shown † that, in a cell with transference, which is reversible to the anion,

$$E_t = -\frac{2n_c\ddagger RT}{nF}\ln\frac{m_1\gamma_1}{m_2\gamma_2} \tag{37}$$

* Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1943; Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931, pages 763-825; MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939, page 167.

† The potentials of the two electrodes and the junction potential are added together for the electromotive force of the whole cell. MacInnes "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939, pages 222–225.

‡ The term $2n_c$ does not appear in the formulas for cells with transference given before because the junction potential was practically eliminated with a potassium chloride bridge. It is assumed in this derivation that n_c remains constant between m_1 and m_2.

Dividing equation 37 by equation 36 gives

$$n_c = \frac{E_t}{E} \tag{38}$$

By using this formula for data obtained in the lithium cell just described, the transference number of lithium ion in 0.01 molal solution was found to be 0.334* in close agreement with the value 0.332 found by other methods.

The Lead Storage Battery. Various combinations of electrodes have been used for converting chemical energy directly into useful electric energy. With two notable exceptions, the lead storage battery and the zinc–ammonium chloride Leclanché dry battery, most of these are no longer used in competition with the cheap electricity now obtainable from large mechanically driven dynamos.

The lead storage battery consists of an electrode of lead and an electrode of lead oxide immersed in sulfuric acid. Each plate has a rough surface exposing a large area, and the two are held close together in rigid frames. The cell is

$$\mathrm{Pb;\ PbSO_4,\ H_2SO_4\ (20\%);\ PbO_2,\ Pb}$$

and the ionic cell reaction is

$$\mathrm{Pb + HSO_4^- = PbSO_4\ (\mathit{s}) + H^+ + 2\mathit{e}}$$

$$\mathrm{PbO_2 + 3H^+ + HSO_4^- + 2\mathit{e} = PbSO_4\ (\mathit{s}) + 2H_2O}$$

$$\mathrm{Pb + PbO_2 + 2H^+ + 2HSO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} 2PbSO_4\ (\mathit{s}) + 2H_2O} \tag{39}$$

The important thing about this cell reaction is the fact that equation 39 can be reversed, and if electrons from a dynamo are put into one electrode, additional spongy lead is deposited from the lead ions in the saturated solution of lead sulfate. According to a hypothetical mechanism, electrons are removed from the other electrode at the same time, thus, converting Pb^{++} from the lead sulfate into Pb^{++++} which in turn deposits as PbO_2 according to the reaction:

$$\mathrm{Pb^{++++} + 4OH^- = PbO_2 + 2H_2O}$$

These electrically replenished electrodes are then ready to follow again the original cell reaction with the flow of electrons from lead electrode to lead oxide electrode, thus generating useful electricity.

* MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920).

When the battery is discharged, the sulfuric acid is converted into lead sulfate and water, whereas the sulfuric acid is regenerated on charging. The specific gravity of the sulfuric acid and water of a fully charged battery is about 1.215. If the battery is allowed to stand idle for a while in a discharged condition, the lead sulfate becomes less soluble and crystallizes out on the electrodes in difficultly removable layers, thus, tending to cover up the electrode and decrease the current attainable. In cold weather the dilute sulfuric acid may freeze, even a few degrees above 0°, as was shown in Fig. 79 on page 325; and such freezing may damage the electrodes and their retaining structures.

The voltage of a cell should not be allowed to fall below 1.8 volt, and the specific gravity should not be allowed to fall too far. When these conditions are reached, the battery should be recharged until gaseous hydrogen and oxygen are copiously evolved, and a constant voltage of a little over 2 volts is reached.

On open circuit there is no reaction, because the high overvoltage of hydrogen on lead prevents chemical action with the acid. Impurities in the lead electrodes or deposits from impure water may set up local action which runs the cell down. Again, some electrical leakage may take place across the cover of the cell, particularly if it has dirt or sulfuric acid on its surface.

REFERENCES

MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939.

Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., New York, 1942.

Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1943.

Dole, "Experimental and Theoretical Electrochemistry," McGraw-Hill Book Co., New York, 1935.

Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, New York, 1938.

Creighton and Koehler, "Principles and Applications of Electrochemistry," John Wiley & Sons, New York, 1935.

PROBLEMS

1. A thallium amalgam of 4.93 per cent Tl in Tl + Hg and another amalgam of 10.02 per cent Tl are placed in separate legs of a glass cell and covered with a solution of thallous sulfate to form a concentration cell. The voltage of the cell is 0.029480 volt at 20° and 0.029971 volt at 30°. The mercury acts only as a diluent. (*a*) Which is the negative electrode? (*b*) What is the heat of dilution per mole of thallium when enough mercury is added to change the concentration from 10.02 per cent to 4.93

per cent? (*c*) What is the electromotive force of the cell at 40°? The experimentally determined values are as follows:

(*a*) 10.02 per cent is negative toward 4.93 per cent.
(*b*) −349 cal per mole.
(*c*) 0.030467 volt.

2. The voltage of the cell,

$$\text{Zn; } ZnCl_2 \text{ (sp. gr. 1.391); HgCl; Hg}$$

is 1.0000 volt at 15° and 1.00047 volts at 20°. What is the average heat of the reaction,

$$\text{Zn } (s) + 2\text{HgCl } (s) = ZnCl_2 \text{ (sp. gr. 1.391)} + 2\text{Hg } (l)$$

between 15° and 20°? *Ans.* $\Delta H = -44{,}865$ cal.

3. The free energy of formation $\Delta F^0_{298.1K}$ of Pb^{++} is −5,630 cal. The free energies of formation of the elements and of hydrogen ion at unit activity are taken as zero. Calculate the voltage of the cell at 25°,

$$\text{Pt, } H_2 \text{ (1 atm); } H^+ (a = 1) \,||\, Pb^{++} (a = 1); \text{ Pb}$$

Ans. −0.122 volt.

4. Given the cell at 25°,

$$\text{Pb; } Pb^{++} (a = 1) \,||\, Ag^+ (a = 1); \text{ Ag}$$

(*a*) calculate the voltage; (*b*) write the cell reaction; and (*c*) calculate the free-energy change.

Ans. (*a*) 0.925 volt.
(*b*) $\frac{1}{2}\text{Pb } (s) + Ag^+ (a = 1) = \frac{1}{2}Pb^{++} (a = 1) + \text{Ag } (s)$.
(*c*) −21,330 cal.

5. (*a*) Construct a cell in which the reaction is

$$\tfrac{1}{2}\text{Cd } (s) + \tfrac{1}{2}Br_2 \ (l) = \tfrac{1}{2}Cd^{++} (a = 1) + Br^- (a = 1)$$

(*b*) What is the voltage of the cell?
(*c*) What is the free energy of the reaction?
(*d*) What difference would there be in the solution of this problem if the reaction were written

$$\text{Cd } (s) + Br_2 \ (l) = Cd^{++} (a = 1) + 2Br^- (a = 1)$$

Ans. (*a*) $\text{Cd; } Cd^{++} (a = 1) \,||\, Br^- (a = 1); \ Br_2 \ (l), \text{ Pt.}$
(*b*) 1.4674 volts.
(*c*) −33,836.
(*d*) (*a*) and (*b*) would be the same; (*c*) would be −67,636.

6. Calculate the voltage of the following cell at 25°:

$$\text{Pt; } Ti^{+++} (a = 0.3), \ Ti^{++++} (a = 0.5) \,||\, Ce^{+++} (a = 0.7), \ Ce^{++++} (a = 0.002); \text{ Pt}$$

Ans. 1.406 volts.

7. Write the reaction of the cell:

$$\text{Pt; } Fe^{++} (a = 1), \ Fe^{+++} (a = 1) \,||\, Ag^+ (a = 1); \text{ Ag}$$

Calculate (*a*) the cell voltage and (*b*) the free energy of the reaction at 25°. (*c*) What is the value of the equilibrium constant? (*d*) What would be the activity

of Ag^{+} ions in equilibrium with solid silver in a solution containing Fe^{+++} and Fe^{++} at unit activity?

Ans. (*a*) $E^0 = 0.028$ volt. (*b*) $\Delta F^0 = -645$ cal. (*c*) $K = 2.97$. (*d*) $a_{Ag+} = 0.34$.

8. Develop a formula for calculating the voltage of a cell consisting of two chlorine electrodes at different pressures immersed in a solution of a chloride. Calculate the voltage if the chlorine of one electrode is at 1 atm, the other is at 0.25 atm, and the temperature is 25°. *Ans.* ± 0.018 volt.

9. To what *p*H are the following hydrogen-ion activities at 25° equal: (*a*) 0.3, (*b*) 10^{-11}? To what hydrogen-ion activities at 25° are the following *p*H values equivalent: (*c*) 10.6, (*d*) -1.1?

Ans. (*a*) 0.52. (*b*) 11. (*c*) 2.5×10^{-11}. (*d*) 12.6.

10. A voltage of 0.829 was obtained at 25° for a solution when placed in the cell:

$$Pt, H_2 \text{ (1 atm)}; \text{ solution } || \text{ normal calomel electrode}$$

What is the *p*H of the solution? *Ans.* 9.29.

11. (*a*) Write the cell reaction, and derive an expression for the electromotive force of the following cell shown in Fig. 110:

$$Hg; Hg_2Cl_2; KCl\ (1\ N)\ ||\ H^+(a); H_2(p), Pt$$

(*b*) At 25° C what is the voltage of the cell if the barometric pressure is 750 mm, the vapor pressure of water above the solution is 23.7 mm, and the *p*H = 3.50? Neglect the depth of immersion of the platinum electrode, and assume that the hydrogen is saturated with water vapor.

Ans. (*a*) $Hg + Cl^- (1\ N\ KCl) + H^+(a) = \frac{1}{2}\ Hg_2Cl_2 + \frac{1}{2}\ H_2(p)$.
(*b*) -0.4862.

12. The cell,

$$\text{Normal calomel electrode } || \text{ (solution quinhydrone) Pt}$$

was found to have an electromotive force of 0.179 volt for a certain solution at 25°. What is the *p*H of the solution? *Ans.* 4.07.

13. What is the voltage of the cell,

$$Zn; ZnSO_4\ (0.01\ m); ZnSO_4\ (0.1\ m); Zn$$

at 25°? For $ZnSO_4$, $n_a = 0.6$, and the activity coefficients of the Zn^{++} ion are 0.23 in 0.1 *m* $ZnSO_4$ and 0.5 in 0.01 *m* $ZnSO_4$. *Ans.* 0.024 volt.

14. For the cell at 25°,

$$Cd, Hg\ (2 \text{ phases}); Cd\ I_2\ (m = 0.1); AgI, Ag$$

Bates (*J. Am. Chem. Soc.*, **63**, 399 [1941]) found $E = 0.35776$. When cadmium iodide is at unit activity, $E^0 = 0.20060$. Calculate the activity coefficient of the cadmium iodide in 0.100 molal solution. *Ans.* 0.107.

15. A solution at 25° contains Ni^{++} ions at an activity of 0.1. If the solution is too acid, hydrogen will be deposited on the cathode instead of nickel. What should be the *p*H of the solution so that the hydrogen will not be liberated until the potential is 0.1 volt greater than the potential required to deposit the nickel? The overvoltage of hydrogen on nickel may be assumed to be 0.2 volt. *Ans.* 2.72.

---

16. A small dry battery of zinc and ammonium chloride weighing 85 g will operate continuously through a 4-ohm resistance for 450 minutes before its voltage falls

below 0.75 volt. The initial voltage is 1.60, and the effective voltage over the whole life of the battery is taken to be 1.00.

Theoretically how many miles above the earth could this battery be raised by the energy delivered by this battery under these conditions?

17. Calculate the electromotive force of the cell,

$$\text{Ag } (s);\ \text{AgCl } (s);\ \text{NaCl } (1\ N);\ \text{Hg}_2\text{Cl}_2\ (s);\ \text{Hg } (l)$$

from the following standard free energies of formation:

Ag^+	+18,488 cal/mole
AgCl (*s*)	−26,187
Na^+	−62,588
Cl^-	−31,367
Hg_2Cl_2	−50,274

18. E for the standard Weston cadmium cell is 1.0186 volts at 20° and decreases 0.0000406 volt for each degree rise in temperature above 20°.

(*a*) State these facts with a single mathematical equation, and calculate (*b*) the heat evolved or absorbed per mole of cadmium consumed, and (*c*) the free-energy change per mole of cadmium consumed.

19. Given the cell at 25°,

$$\text{Pt, Cl}_2\ (g);\ \text{Cl}^-\ (a = 1)\ ||\ \text{Tl}^{+++}\ (a = 1),\ \text{Tl}^+\ (a = 1);\ \text{Pt}$$

(*a*) Write the cell reaction.

(*b*) Calculate ΔF^0.

(*c*) Calculate the equilibrium constant for the cell reaction.

(*d*) Calculate E for the cell when the chloride ion activity is 0.1 instead of 1.

20. (*a*) Construct a cell in which the reaction is

$$\tfrac{1}{2}\text{Cl}_2\ (g\ 1\ \text{atm}) + \text{Br}^-\ (a = 1) = \text{Cl}^-\ (a = 1) + \tfrac{1}{2}\text{Br}_2\ (l)$$

(*b*) Determine the voltage at 25° and (*c*) calculate the free energy of the reaction.

21. (*a*) Calculate the voltage of the following cell at 25°:

$$\text{Zn};\ \text{Zn}^{++}\ (a = 0.0004)\ ||\ \text{Cd}^{++}\ (a = 0.2);\ \text{Cd}$$

(*b*) Write the cell reaction.

(*c*) Calculate the value of the free-energy change involved in the reaction of the solutions as given, that is, Zn^{++} at an activity of 0.0004 and Cd^{++} at an activity of 0.2.

22. (*a*) Calculate the equilibrium constant for the reaction at 25°:

$$\text{Sn}^{++++} + 2\text{Ti}^{+++} = 2\text{Ti}^{++++} + \text{Sn}^{++}$$

(*b*) When 0.01 mole of stannous ion is added to 1.0 mole of Ti^{++++} ion in 1000 g of water, what will be the concentration of Ti^{+++} ions (if it is assumed for the calculation that the activities are essentially equal to the concentrations)?

23. The electromotive force of the cell,

$$\text{Normal calomel electrode}\ ||\ \begin{pmatrix}\text{FeCl}_3\ (0.1\ m)\\ \text{FeCl}_2\ (0.1\ m)\\ \text{HCl}\ (0.1\ m)\end{pmatrix};\ \text{Pt}$$

is 0.446 volt at 25°. The hydrochloric acid is added to prevent hydrolysis. Assuming that the activity coefficients of the Fe^{+++} and Fe^{++} ions are 0.75 and 0.87

respectively, calculate the value of E^0 for the ferric–ferrous electrode containing 0.1 m HCl.

24. Calculate the voltage at 30° of a concentration cell composed of two amalgams, one having 0.3315 per cent by weight of thallium in Tl + Hg and the other 1.704 per cent by weight of thallium. The density of the first is 13.51 and that of the second 13.48. The experimentally determined voltage of the cell is 0.046937. The difference between the observed and calculated values is due to the fact that the amalgams are so concentrated that they do not behave as ideal solutions.

25. (*a*) What is the activity of hydrogen ions in a solution which has a pH of 8.6 at 25°?

(*b*) Calculate the pH of a solution which has a hydrogen-ion activity of 5.1 equivalents per 1000 g of water at 25°.

26. Calculate the pH of 0.01 N sodium hydroxide solution at 25°. The activity coefficient is 0.75.

27. When the pH of a solution is measured by means of a hydrogen electrode against a calomel electrode, the partial pressure of the hydrogen is usually not exactly 1 atm. At 25° how low can the partial pressure of the hydrogen be before a correction is necessary, if an error of 0.005 pH unit is allowable?

28. What is the potential of the cell,

$$\text{Ag; } AgNO_3 \text{ (0.02 } m\text{); } AgNO_3 \text{ (0.1 } m\text{); Ag}$$

at 25°? For $AgNO_3$, $n_a = 0.53$, and the activity coefficients of silver nitrate are 0.86 in 0.02 m $AgNO_3$ and 0.72 in 0.1 m $AgNO_3$.

29. The cell,

$$\text{K (amalgam); KCl (0.05 } m\text{); AgCl, Ag, AgCl; KCl (0.2 } m\text{); K (amalgam)}$$

is reversible to both cation and anion. Calculate its potential at 25°, knowing the activity coefficients of potassium chloride.

30. What must be the concentration of Cu^{++} ions in order that the deposition potential of copper from solution at 25° will be the same as the deposition potential of zinc from a solution containing Zn^{++} ions at unit activity?

---

31. The voltage of the cell,

$$Pb;\ PbSO_4;\ Na_2SO_4 \cdot 10H_2O \text{ (sat.)};\ Hg_2SO_4;\ Hg$$

is 0.9647 at 25°. The temperature coefficient is 0.000174 volt per degree. Calculate (*a*) the heat of the reaction and (*b*) the free-energy change of the reaction,

$$Pb\ (s) + Hg_2SO_4\ (s) = PbSO_4\ (s) + 2Hg\ (l)$$

32. Calculate ΔF for the reduction with iron of one mole of ferric ion to ferrous ion, each at unit activity.

33. Given the cell at 25°,

$$Cd;\ Cd^{++}\ (a = 1) \,||\, I^-\ (a = 1);\ I_2\ (s),\ Pt$$

(*a*) calculate E^0; (*b*) write the cell reaction; (*c*) calculate ΔF^0.

34. Instead of using oxidation potentials such as Na; $Na^+ = 2.7139$ it would be equally satisfactory to use reduction potentials such as Na^+; Na $= -2.7139$. Recalculate example 5 on page 449 using this system of reduction potentials.

35. Calculate the activity of mercurous ion in a solution at 25° which originally had an activity of 0.001 of mercuric ion after enough ferrous iron has been added to give the solution an activity of ferrous ion equal to 0.0004.

36. (*a*) How should a cell be constructed in order to determine E^0 for the cell corresponding to the reaction of Cl_2 with Fe^{++}? (*b*) What is the equilibrium constant for the reaction?

37. At 25° for the reaction,

$$2Fe^{+++} + 2Hg = 2Fe^{++} + Hg_2{}^{++}$$

the equilibrium constant is 0.018, and at 35° it is 0.054. What is the value of E^0 at 45° for the cell which corresponds to this reaction?

38. Given the cell at 25°,

$$\text{Pt, } X_2;\ X^-\ (a = 0.1)\ ||\ X^-\ (a = 0.001);\ X_2,\ \text{Pt}$$

where X is an unknown halogen:

(*a*) Write the cell reaction.

(*b*) Which electrode is negative?

(*c*) What is the voltage of the cell?

(*d*) Is the reaction spontaneous?

39. What is the activity of zinc ions in a solution which gives with a zinc electrode a voltage of −0.7500 against the standard hydrogen electrode? What is the molality of the solution if the activity coefficient for the zinc ion is 0.30 at this concentration?

40. A hydrogen electrode and a normal calomel cell give a voltage of 0.480 when placed in a certain solution at 25°. What is the *p*H of the solution?

41. A hydrogen electrode and calomel cell are used to determine the *p*H of a solution on a mountain where the barometer is 500 mm. The hydrogen is allowed to bubble out of the electrode at the atmospheric pressure prevailing there. If the *p*H is calculated to be 4.00, what is the correct *p*H of the solution?

42. The cell,

$$\text{Normal calomel electrode}\ ||\ \text{(solution, quinhydrone) Pt}$$

was found to have a potential of 0.212 for a certain solution at 25°. What is the *p*H of the solution?

43. Write each electrode reaction and the net reaction for the cell,

$$\underset{m_1}{\text{Ag; AgCl, LiCl; Li(Hg)}_x;}\ \underset{m_2}{\text{LiCl, AgCl; Ag}}$$

and show that equation 36 follows from equation 8.

44. Calculate the activity of H_2SO_4 in 0.01 molal solution if the activity coefficient γ is 0.545.

45. Tartar, Newschwander, and Ness (*J. Am. Chem. Soc.*, **63**, 28 [1941]) found that the electromotive force of the cell,

$$\text{Pt, } H_2;\ H_2SO_4\ (m = 1.0),\ ZnSO_4\ (m = 0.5);\ Hg_2SO_4;\ \text{Hg}$$

is 0.67281 volt at 25°. $E^0 = 0.61515$ volt. Calculate the activity coefficient of sulfuric acid in a solution which is 1 molal with respect to H_2SO_4 and 0.5 molal with respect to $ZnSO_4$.

---

46. Manganese dioxide electrode has been used for measuring *p*H. Write an equation for the electrode reaction, and give a formula for its use as an indicator of *p*H.

47. The electromotive force of the cell,

$$Hg;\ Hg_2Br_2\ (sat.),\ MBr\ (aq\ soln);\ AgBr\ (sat.);\ Ag$$

has been determined accurately by Dakin and Ewing (*J. Am. Chem. Soc.*, 62, 2280 [1940]), and the values of $E^0_{Ag,\ AgBr}$ have been determined by Owen and Foering (*J. Am. Chem. Soc.*, 58, 1575 [1936]). The data are as follows:

Temp.	E_{cell}	$E^0_{Ag,\ AgBr\ (sat.)}$
15	0.06492	0.07586
25	0.06804	0.07121
35	0.07116	0.06591

(*a*) Calculate $E^0_{Hg_2Br_2;\ Hg}$ at each temperature and find formulas which give E_{cell} and $E_{Hg_2Br_2\ (sat.);\ Hg}$ as a function of temperature.

(*b*) Calculate ΔF^0 at 25° for the reaction,

$$2Ag + Hg_2Br_2 = 2AgBr + 2Hg$$

(*c*) Calculate ΔH for this reaction.

(*d*) Calculate ΔS for this reaction.

(*e*) Using the free energy of formation of silver bromide $\Delta F^0 = -22{,}935$ cal per mole, show that free energy of formation of mercurous bromide is $-42{,}733$.

48. Five hundred milliliters of 0.001 *N* stannous ion is added to 500 ml of 0.001 *N* ferric ion at 25°. What will be the concentration of each of the four resulting ions? The activities may be considered equal to the concentrations for this calculation.

49. A recently developed cell known as the RMR cell is composed of zinc, potassium hydroxide, water, and mercuric oxide. Write an over-all reaction for the cell in which zinc and potassium hydroxide are consumed, mercury is deposited, and potassium zincate is formed, and write the reactions occurring at the two electrodes.

50. A solution 0.5 molal with respect to H_2SO_4, and 1.5 molal with respect to zinc sulfate has a vapor pressure of 22.454 mm at 25°. For the cell,

$$Pt,\ H_2;\ H_2SO_4\ (m = 0.5);\ ZnSO_4\ (m = 1.5);\ Hg_2SO_4;\ Hg$$

$E = 0.69021$ volt and E^0 is equal to 0.61515 volt. For the cell

$$Zn;\ H_2SO_4\ (m = 0.5);\ ZnSO_4\ (m = 1.5);\ Hg_2SO_4;\ Hg$$

$E = 1.44561$ volts and $E^0 = 1.3765$ volts. The vapor pressure of pure water at 25° is 23.75 mm. (*a*) Calculate the activity of the water. (*b*) Calculate the mean activity of the sulfuric acid, and (*c*) the mean activity of the zinc sulfate.*

* Tartar, Newschwander, and Ness, *J. Am. Chem. Soc.*, **63**, 28 (1941).

CHAPTER XVII

IONIC EQUILIBRIA

The study of equilibria involving ions in solution constitutes one of the oldest branches of physical chemistry. It was shown on pages 248 and 397 that salts and other electrolytes dissociate into electrically charged ions, when they are dissolved in water, but further discussion of the equilibria of ions was postponed in order to present first the concepts of chemical equilibrium, the facts of electrolytic conductance, and the significance of electromotive-force measurements.

Ionization of Weak Electrolytes. The extent to which a weak electrolyte is dissociated may be determined in different ways, among which the electrical-conductance method is the most used on account of its accuracy and simplicity. In general, the dissociation becomes greater as the solution is diluted. The recombination of the ions decreases because the number of collisions becomes less. If the solute is not dissociated at all, the solution will have a conductance no greater than that of the solvent alone. If it is completely dissociated, the equivalent conductance cannot be increased any more by further dilution.

According to the simplest point of view, the degree of dissociation α of a weak electrolyte can be calculated from the conductance of the electrolyte and the equivalent conductance at infinite dilution as was first done by Arrhenius. It has been shown that at infinite dilution the equivalent conductance Λ_0 is equal to the sum of the ionic conductances l_c and l_a of the cation and anion.

$$\Lambda_0 = l_c + l_a \tag{1}$$

If the change in velocity of the ions with concentration is neglected and it is assumed that the only influence of dilution on the equivalent conductance of a weak electrolyte is the production of more ions, it may also be assumed that, for an electrolyte dissociating into two ions,

$$\Lambda = \alpha l_c + \alpha l_a = \alpha(l_c + l_a) \tag{2}$$

where Λ is the equivalent conductance, that is, the conductance of a gram equivalent of the electrolyte at the specified dilution, l_c and l_a are the equivalent conductances of the cation and anion, and α is the de-

gree of dissociation. If one equivalent of electrolyte is present in solution, there will be α equivalents of each ion.

Dividing equation 2 by equation 1 gives

$$\alpha = \frac{\Lambda}{\Lambda_0} \qquad (3)$$

Although satisfactory for weak electrolytes, this equation cannot be applied to strong electrolytes in which dissociation is practically complete. The change of equivalent conductance of strong electrolytes with concentration is due to a change in velocity of the ions, as described later in this chapter.

Acetic acid is a good example of a weak electrolyte. When dissolved in water, it dissociates according to the reaction:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

If c moles of acetic acid is dissolved in a liter of water and the degree of dissociation of the acid is α, then the concentration of hydrogen ions is $c\alpha$, the concentration of acetate ions is $c\alpha$, and the concentration of unionized acetic acid molecules is $c(1 - \alpha)$. The equilibrium or ionization constant K is given by the expression:

$$K = \frac{c_{H^+} \times c_{CH_3COO^-}}{c_{CH_3COOH}} = \frac{c\alpha \times c\alpha}{c(1 - \alpha)} = \frac{\alpha^2 c}{1 - \alpha} \qquad (4)$$

If more than two ions are formed, the ionization constant will have a different form which may be easily derived.

Example 1. The equivalent conductance of a 0.001028 *N* acetic acid solution is found to be 48.15 at 25°. The equivalent conductance at infinite dilution is 390.7. Calculate the degree of dissociation of acetic acid at this concentration, and calculate the ionization constant.

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{48.15}{390.7} = 0.1232$$

$$K = \frac{\alpha^2 c}{1 - \alpha} = \frac{(0.1232)^2 \times 0.001028}{0.8768} = 1.780 \times 10^{-5}$$

From calculations like this, Table I is obtained by using the data of MacInnes and Shedlovsky.*

* MacInnes and Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429 (1932); MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939, page 56.

TABLE I

IONIZATION CONSTANT OF ACETIC ACID AT 25°

($\Lambda_0 = 390.7$)

Concentration, equivalents/liter	Equivalent Conductance	Degree of Dissociation	K, Dissociation Constant $\times 10^5$
0.00002801	210.4	0.5385	1.760
0.0001532	112.0	0.2867	1.767
0.001028	48.15	0.1232	1.781
0.002414	32.22	0.08247	1.789
0.005912	20.96	0.05365	1.798
0.01283	14.37	0.03678	1.803
0.05000	7.36	0.01884	1.808

The value of K calculated in this way is reasonably constant, and it is satisfactory for most practical work. There are, however, unsatisfactory assumptions involved in this calculation which are partly compensating. Making a correction for the fact that the ionic conductances are not quite the same as they are at infinite dilution and estimating the activity coefficients of the ions from the Debye–Hückel theory discussed later in this chapter on page 511, MacInnes * shows that these dissociation constants have values ranging from 1.752 at 0.0002801 N to 1.721 at 0.05000 N. In this revised calculation Λ_0 for acetic acid is not used, but a value of the equivalent conductance for complete dissociation is obtained at the given concentration by subtracting Λ_{NaCl} from the sum of Λ_{HCl} and $\Lambda_{NaC_2H_3O_2}$ at these concentrations, it being assumed that these electrolytes are completely dissociated.

With the help of equation 4 it is possible to calculate at any concentration c the degree of dissociation of acetic acid or any other weak electrolyte which dissociates into two ions. When the electrolyte is weak, that is, K is 10^{-4} or 10^{-5} or less, the concentration of undissociated electrolyte is practically that of the original concentration.

Example 2. Calculate the concentration of hydrogen ions in a solution which contains 0.0700 mole of acetic acid in 500 ml of water solution. It is convenient to convert the data into terms of moles per liter. The original concentration c_0 is then 0.140 mole per liter. Let x equal the number of moles of acetic acid

* MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp. New York, 1939, pages 342–348.

ionized per liter, and assume that for weak acids $c_0 - x$ is essentially equal to c_0. Approximately,

$$K = 1.80 \times 10^{-5}$$

$$= \frac{c_{H^+} \times c_{C_2H_3O_2^-}}{c_{HC_2H_3O_2}} = \frac{x^2}{c_0} = \frac{x^2}{0.140}$$

$$x^2 = 1.80 \times 10^{-5} \times 0.140 = 2.52 \times 10^{-6}$$

$$x = 1.59 \times 10^{-3}$$

More exactly:

$$c_{HC_2H_3O_2} = (c_0 - x) \quad \text{and} \quad x^2 = 1.80 \times 10^{-5}(0.140 - x)$$

$$x^2 + 1.8 \times 10^{-5}\, x - 2.52 \times 10^{-6} = 0$$

$$x = 1.58 \times 10^{-3}$$

Although these formulas are derived on the assumption that the electrolytes dissociate into only two ions, as a matter of fact they apply fairly well also to di- and tribasic acids because they dissociate in steps. The first hydrogen atom ionizes much more readily than the second or third hydrogen in a polybasic acid. Thus, in the electrolytic dissociation of carbonic acid, the first hydrogen ion comes off according to the reaction,

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

in which

$$K = 4.54 \times 10^{-7}$$

but the second hydrogen ion has to pull away from an ion with two negative charges instead of one. Accordingly, the degree of dissociation is considerably less, and the dissociation constant is smaller; thus:

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--} \qquad K = 5.61 \times 10^{-11}$$

Ionization constants for a number of acids are given in Table II.

The dissociation of bases to give hydroxyl ions has also been the subject of extensive study. The alkali and alkaline-earth hydroxides are very strong bases and are dissociated to about the same extent as equivalent solutions of hydrochloric and nitric acids, whereas, on the other hand, ammonia and many of the organic bases are very weak. Table III gives the ionization constants of several typical bases.

The ionization of bases and acids may be determined experimentally in several different ways: from measurements of electrical conductance or of electromotive force, from measurements of the concentration of the hydrogen or hydroxyl ions as described in Chapter XVI, and from measurements of the rate of reactions catalyzed by these ions. For

example, the rate of inversion of cane sugar provides a means of determining the concentration of hydrogen ions, and the rate of condensation of acetone enables one to determine the concentration of hydroxyl ions.

TABLE II

IONIZATION CONSTANTS OF ACIDS IN WATER AT 25°

Acid	Ionization Constant
Trichloroacetic acid, CCl_3COOH	2×10^{-1}
Iodic, HIO_3	2×10^{-1}
Dichloroacetic, $CHCl_2COOH$	5.2×10^{-2}
Monochloroacetic, $CH_2ClCOOH$	1.55×10^{-3}
Formic, $HCOOH$	2.1×10^{-4}
Acetic, CH_3COOH	1.8×10^{-5}
Carbonic K_1, H_2CO_3	4.54×10^{-7}
K_2, HCO_3^-	5.61×10^{-11}
Hydrocyanic acid, HCN	7.2×10^{-10}
Boric K_1, H_3BO_3	5.8×10^{-10}
K_2, $H_2BO_3^-$	2×10^{-13}
K_3, HBO_3^{--}	2×10^{-14}
Water, H_2O	1.8×10^{-16}
Ethane, C_2H_6	Approx. 10^{-34}

TABLE III

IONIZATION CONSTANTS OF BASES AT 25°

Base	Ionization Constant
Guanidine	3×10^{-1}
Piperidine	1.3×10^{-3}
Methylamine	4.0×10^{-4}
Trimethylamine	6.2×10^{-5}
Ammonia	1.8×10^{-5}
Pyridine	1.6×10^{-9}
Aniline	5.1×10^{-10}

In comparing the acidity of different acids, it is the hydrogen-ion concentration which is significant. In weak acids this is proportional to the square root of the dissociation constants as shown in equation 5.

The equilibrium constant K can be simplified when α is small because $(1 - \alpha)$ does not differ appreciably from unity; thus,

$$K = \frac{\alpha^2 c}{(1 - \alpha)} \cong \alpha^2 c$$

then,

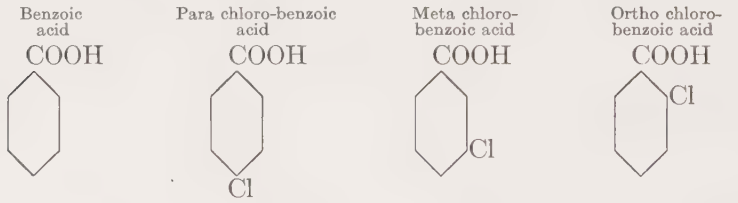
$$\alpha = \sqrt{\frac{K}{c}} \tag{5}$$

Example 3. Compare the acidity of monochloroacetic acid with that of acetic acid at 25°.

$$\frac{\alpha_{CClH_2COOH}}{\alpha_{CH_3COOH}} = \frac{\sqrt{K_{CClH_2COOH}/c}}{\sqrt{K_{CH_3COOH}/c}} = \frac{\sqrt{0.00155}}{\sqrt{0.0000180}} = 9.3$$

In example 3 it is seen that replacing one of the hydrogen atoms on the first carbon with the negative chlorine atom makes it 9.3 times as easy for the hydrogen of the carboxyl group to break away and form a hydrogen ion. Apparently, the attraction of chlorine for electrons pulls the electron pair farther away from the hydrogen of the carboxyl and permits the hydrogen ion to leave with the expenditure of less energy. The substitution of more hydrogen atoms by chlorine in acetic acid decreases the energy with which the hydrogen ion is held and gives acids with larger ionization constants, as is shown by comparing acetic acid with mono-, di-, and trichloroacetic acids shown in Table II.

The influence of one atom or group on the reactivity of a near-by atom is affected by the distance and the position as shown in the chloro-substituted benzoic acids at 25°.



$K = 0.000073$ $K = 0.000093$ $K = 0.000155$ $K = 0.00132$

In these examples the reactivity of the molecule is characterized by the ease with which a hydrogen ion is released. Many other properties such as relative rates of chemical reaction with specific reactants are used to determine the influence of substituents and molecular structure on reactivity. These relations are being correlated now in terms of the electron theory of valence so that good predictions can often be made on the basis of molecular structure concerning equilibria and rates of reaction. The electron theory is discussed in many texts in organic chemistry.*

Repression of Ionization by Salts. Just as the dissociation of a gaseous substance is diminished by the addition of an excess of one of the products of dissociation, so the ionization of a weak acid is repressed by the

* Such, for example, as J. Johnson's chapter 25 in Gilman's "Organic Chemistry," John Wiley & Sons, New York, 1943, and Remick, "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, New York, 1943.

addition of a salt formed from the acid and a strong base. The salts are almost completely dissociated, and the addition of the extra anions drives the equilibrium back to give more undissociated acid. For example, a solution of a weak acid HA is made much less acid by the addition of the sodium salt of the acid. The quantitative treatment follows for the reactions,

$$HA \rightleftharpoons H^+ + A^- \quad \text{and} \quad NaA \rightleftharpoons Na^+ + A^-$$

The concentration of the salt is represented by c_s. Since salts are generally completely ionized, c_s is also the concentration of the ions produced by the ionization of the salt. The total concentration of the weighed-out acid HA, including both undissociated and dissociated acid, is designated by c_0, and the degree of dissociation of the acid is designated by α_0. The concentration of the undissociated acid is represented by c_{HA}. Then,

$$c_{H^+} = \alpha_0 c_0; \qquad c_{A^-} = \alpha_0 c_0 + c_s$$

and

$$c_{HA} = (1 - \alpha_0)c_0$$

$$K = \frac{c_{H^+}c_{A^-}}{c_{HA}} = \frac{\alpha_0 c_0 \times (\alpha_0 c_0 + c_s)}{(1 - \alpha_0)c_0}$$

For weak acids α_0 is so small that $\alpha_0 c_0$ is negligible in comparison with c_s; and $1 - \alpha_0$ is practically equal to unity. Then,

$$K = \alpha_0 c_s$$

or

$$\alpha_0 = \frac{K}{c_s} \tag{6}$$

In other words, the degree of ionization of a weak acid in the presence of a salt containing a common ion is approximately independent of the concentration of the acid, and it is inversely proportional to the concentration of the added salt.

Example 4. In example 2 it was calculated that 0.140 mole of acetic acid per liter gave a hydrogen-ion concentration of 1.58×10^{-3} gram ions per liter. If 0.1 mole of solid sodium acetate is dissolved in a liter of this solution, approximately what will be the concentration of hydrogen ions, if it is assumed that the volume of the solution remains practically unchanged?

$$K = 1.80 \times 10^{-5} = \frac{c_{H^+} \times c_{C_2H_3O_2^-}}{c_{HA}} = \frac{c_{H^+} \times 0.100}{0.140}$$

$$c_{H^+} = \frac{1.80 \times 10^{-5} \times 0.14}{0.100} = 2.52 \times 10^{-5}$$

Similar considerations hold for the addition of a salt to a weak base, thus making the solution less basic. Practical use is made of this repression of ionization. For example, certain metal hydroxides, such as magnesium hydroxide, are precipitated by ammonium hydroxide, but, when ammonium chloride is added, the ionization of ammonium hydroxide becomes so slight that there are not then enough hydroxyl ions to precipitate the magnesium as hydroxide.

Ionization of Water. Water is a weak electrolyte with an ion product of 1.0×10^{-14} at 25°, dissociating according to the reaction:

$$HOH \rightleftharpoons H^+ + OH^-$$

The ion product of water has been carefully determined by several different methods, all of which are in excellent agreement.

Example 5. Calculate the degree of dissociation and the ion product of water at 25° from the fact that the specific conductance of the purest water has been found to be 5.5×10^{-8} * $ohm^{-1}\ cm^{-1}$. The ionic conductances at infinite dilution are $l_{H^+} = 349.8$ and $l_{OH^-} = 198$.

In pure water 18 ml contains 1 gram equivalent of H_2O. Then, the equivalent conductance Λ is given by the relation:

$$\Lambda = LV = 5.5 \times 10^{-8} \times 18 = 9.9 \times 10^{-7}$$

$$\Lambda_0 = l_c + l_a = 349.8 + 198 = 547.8$$

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{9.9 \times 10^{-7}}{547.8} = 1.81 \times 10^{-9}$$

The value 547.8 is the equivalent conductance of a hypothetical completely ionized water.

Since there are 1000/18 or 55.5 moles of water per liter,

$$c_{H^+} = c_{OH^-} = 55.5\alpha = 55.5 \times 1.81 \times 10^{-9} = 1.00 \times 10^{-7}$$

$$K = \frac{c_{H^+} \times c_{OH^-}}{c_{H_2O}} = \frac{(1.00 \times 10^{-7})^2}{55.5} = 1.8 \times 10^{-16}$$

Since the concentration of water in the denominator remains constant, it is usually absorbed into the ionization constant, and the *ion product* K_w is commonly used. It is defined as follows:

$$K_w = c_{H^+} \times c_{OH^-} = 1.00 \times 10^{-7} \times 1.00 \times 10^{-7} = 1.00 \times 10^{-14}$$

Example 6. Determine the ion product of water at 25° from the following data. The electromotive force of the following cell at 25° is 1.05033 volt.†

$$(Pt)\ H_2\ (1\ atm);\ KOH\ (0.01\ m),\ KCl\ (0.01\ m);\ AgCl;\ Ag$$

* Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 317 (1894); Jones and Bradshaw, *J. Am. Chem. Soc.*, **55**, 1800 (1933).

† Harned and Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).

The standard electrode potential E^0 for the cell,

$$\text{Pt, } H_2\text{; HCl } (a = 1)\text{; AgCl; Ag}$$

is 0.22239 volt at 25°.*

$$K_w = \gamma_{H^+} c_{H^+} \gamma_{OH^-} c_{OH^-}$$

The cell reaction in both cases is $\frac{1}{2}H_2 + AgCl = H^+ + Cl^- + Ag$. Hence,

$$1.05033 = 0.22239 - \frac{RT}{nF} \ln \gamma_{H^+} c_{H^+} \times \gamma_{Cl^-} c_{Cl^-}$$

$$= 0.22239 - \frac{RT}{nF} \ln \left[K_w \times \frac{\gamma_{Cl^-} c_{Cl^-}}{\gamma_{OH^-} c_{OH^-}} \right]$$

$$= 0.22239 - 0.05915 \log \left[K_w \times \frac{\gamma_{Cl^-} \times 0.01}{\gamma_{OH^-} \times 0.01} \right]$$

In this dilute solution, $\gamma_{Cl^-} = \gamma_{OH^-}$ very closely, although it is not accurate enough to assume that they equal unity. Hence,

$$\log K_w = \frac{-1.05033 + 0.22239}{0.05915} = -13.997 = \overline{14}.003$$

$$K_w = 1.01 \times 10^{-14}$$

Direct determinations of the ion product of water have been made also by measuring the catalytic effects of H^+ and OH^- on the rates of certain organic reactions. Another method involves the measurement of the hydrolysis of salts, as illustrated in example 10. The ionization of water is given at various temperatures in Table IV.

TABLE IV

Ion Product of Pure Water [1]

Temperature	0°	10°	25°	40°	50°
$K_w \times 10^{14}$	0.113	0.292	1.008	2.917	5.474

[1] Harned and Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).

The correctness of the data of Table IV can be checked further by taking the values of the ionization constant of water at two temperatures and calculating the heat of the reaction,

$$H_2O = H^+ + OH^-$$

* Harned and Ehlers, *J. Am. Chem. Soc.*, **54**, 1350 (1932).

Introducing the values for 10° and 40° into the equation

$$\Delta H = \frac{2.303R(\log K_2 - \log K_1)T_2T_1}{T_2 - T_1}$$

and solving for ΔH, we obtain 13.5 kcal. This value agrees well with that found for the reverse reaction by the direct calorimetric measurement of the heat of neutralization of completely ionized acids and bases, namely, -13.8 kcal.

Thus, in dilute solutions, when a strong base such as NaOH, KOH, or LiOH is neutralized with a strong acid such as HCl or HNO_3, the heat evolved is always about the same. This constancy in the heat of neutralization is easily explained by the ionization theory. Since all the reactants and all the products are completely ionized, the sodium or potassium ions and the chloride or nitrate ions remain unchanged; and the only chemical reaction is

$$OH^- + H^+ = H_2O \qquad \Delta H = -13.8 \text{ kcal}$$

Strictly speaking, the ions are hydrated, for example, $(H_3O)^+ \cdot xH_2O$ and $OH^- \cdot yH_2O$. It thus appears that the neutralization of a strong acid by a strong base in dilute solution consists in the combination of hydrated hydrogen and hydroxyl ions to form undissociated water. The heat of this ionic reaction is -13.8 kcal. The heat of formation of water from its hydrated ions must not be confused with the heat of formation of water from its elements, nor with the heat of combination of unhydrated ions.

When weak acids or bases are neutralized, not only is the heat of neutralization of H^+ and OH^- ion evolved, but, also, heat is absorbed in dissociating the weak acid or base. The resulting salts are usually completely ionized. For example, the neutralization of HCN by NaOH evolves only 2.9 kcal, whereas 13.8 kcal would be evolved if the acid were completely ionized. The difference 10.9 kcal represents the heat absorbed in ionizing hydrocyanic acid in water.

Heats of ionic reactions including neutralizations are determined simply in a calorimeter. When zinc deposits copper from a copper sulfate solution, for example,

$$Zn + Cu^{++} \rightleftharpoons Cu + Zn^{++} \qquad \Delta H = -53 \text{ kcal}$$

When dilute solutions of ions are mixed, there is no thermal change unless a reaction takes place. For example, when dilute solutions of sodium bromide and sodium nitrate are mixed, no heat is evolved or absorbed. However, when sodium bromide and silver nitrate are

mixed, there is an evolution of 20 kcal per mole due to the heat of precipitation of silver bromide. Moreover, in dilute solutions the heat of precipitation of silver bromide is the same at the same temperature whether the starting materials were potassium bromide and silver sulfate or any other ionized bromide and ionized silver salt.

It is possible to prepare a table of heats of formation of the different positive and negative ions from which heats of ionic reaction can be calculated. The heat of the reaction $\frac{1}{2}H_2 = H^+ + e$ is usually taken arbitrarily as zero, and the heats of formation of other ions are then obtained by difference from known ionic reactions.

Proton Theory of Acids. Certain general aspects of the behavior of acids and bases were overlooked in the early development of physical chemistry because of the importance of water and its solutions, and because of the successes of the Arrhenius theory. Thus, according to an older viewpoint, only aqueous solutions show acid and basic properties, and the term neutralization refers to the combination of hydrogen ions and hydroxyl ions. But the formation of water is not a necessary criterion for neutralization. For example, the following reactions,

$$HCl + NH_3 = NH_4Cl \quad \text{(in benzene)}$$

and

$$HCl + NaC_2H_3O_2 = HC_2H_3O_2 + NaCl \quad \text{(in glacial acetic acid)}$$

give the usual neutralization curve with electrometric titration.

In 1923 under the leadership of Brönsted and Bjerrum in Denmark, as well as Lowry in England and others, the proton theory of acids and bases was proposed.* A proton is a hydrogen atom which has lost its electron, leaving a small nucleus with a mass a little over 1 on the atomic weight scale and with one positive charge. This tiny unit 10^{-13} cm in diameter immediately attracts solvent molecules and becomes "solvated." According to this theory, acids and bases are uniquely characterized by a tendency to exchange protons, just as oxidizing and reducing agents are uniquely characterized by a tendency to exchange electrons. There is much in common between these two systems. For example, a given material may be a reducing agent with respect to another one which is lower in the electromotive series, but it may be an oxidizing agent toward a substance higher in the series. In the same way a given substance may be an acid with respect to a substance of greater

* Hall, *J. Chem. Education*, **12**, 124 (1940).

A complete discussion of the theory of acids is given in "Contributions to Chemical Education 1," entitled "Acids and Bases," *J. Chem. Education*, Easton, Pa. 1941. A bibliography is given by Alyea, *J. Chem. Education*, **16**, 535 (1939).

base strength, or it may act as a base toward a substance of lesser base strength.

According to this very simple view, *an acid is a substance which has a measurable tendency to give up protons* (H^+ ions). Thus, any compound which contains hydrogen may conceivably act as an acid, but, in methane and in hydride ion (H^-) and similar compounds, the tendency to give protons is so extremely small (that is, the force holding the proton is so great) that the substances can hardly be classed as acids.

The *strength of an acid* is the quantitative measure of its tendency to release protons. It varies with the solvent and the experimental conditions and is determined by the electronic and nuclear structure of the acid. Thus, HI is intrinsically a stronger acid than HF because its internuclear distance is greater and the proton is held less firmly, and $HMnO_4^-$ is intrinsically weaker than $HMnO_4$ because the negative charge tends to prevent the escape of the positive proton.

An uncharged acid cannot of itself separate into a positive proton and negative anion; energy must be supplied from somewhere. This energy may come from a chemical reaction such as the combination between the proton and the solvent.

According to the simplest view, an acid A dissociates as follows,

$$A = H^+ + B$$

where B is a *base*, defined by Brönsted as a substance which takes up protons; but, according to a more nearly complete picture, it is necessary to include something to react further with the free proton, providing energy for the liberation of the proton from the acid. Thus,

$$A_1 + \text{solvent} = H^+\cdot\text{solvent} + B_1 \tag{7}$$

But, since

$$H^+\cdot\text{solvent} = H^+ + \text{solvent}$$

$H^+\cdot$solvent may be regarded as an acid A_2 and the solvent as a base B_2. Then rewriting equation 7, we have

$$A_1 + B_2 = A_2 + B_1 \tag{8}$$

Hydrochloric acid in water may be taken as a specific example.

$$\underset{A_1}{HCl} + \underset{B_2}{HOH} = \underset{A_2}{H^+\cdot H_2O} + \underset{B_1}{Cl^-}$$

This theory emphasizes the similarity between all such processes as the following:

Acid		Base	+ Proton
NH_4^+	$\rightleftharpoons$	NH_3	$+ H^+$
H_2O	$\rightleftharpoons$	OH^-	$+ H^+$
HSO_4^-	$\rightleftharpoons$	$SO_4^{=}$	$+ H^+$
$HPO_4^{=}$	$\rightleftharpoons$	$PO_4^{\equiv}$	$+ H^+$
$HFe(CN)_6^{\equiv}$	$\rightleftharpoons$	$Fe(CN)_6^{==}$	$+ H^+$
$Cr(H_2O)_6^{+++}$	$\rightleftharpoons$	$Cr(H_2O)_5OH^{++}$	$+ H^+$
$C_6H_4(NH_3)_2^+$	$\rightleftharpoons$	$H_2NC_6H_4NH_3^+$	$+ H^+$

All these reactions take place in water solution to an easily measurable extent, because water acts as a *base* and forms the hydrated proton. The hydrated proton is often called the hydronium ion (H_3O^+). The extent to which these reactions run in different solvents depends on the base strength of the solvent, that is, the ability of the solvent to attach protons. Thus, at equal concentrations all the dissociations would be very complete in the solvent liquid ammonia and very incomplete in the solvent acetic acid. The solvent ammonia has a much greater attraction for protons than has the solvent acetic acid.

Dissociation of a dissolved acid into protons occurs by combination with the solvent, and the result of this solvolysis is to diminish the acidity since a weaker acid is always formed by interaction with the solvent; that is, the proton is held more tightly. According to this view, HCl is actually very acid in benzene in which the solvation of the proton is slight, less acid in water in which it is more solvated, and still less acid in ammonia in which the union of the proton with the solvent must be still more complete.

A still more general theory of acids has been proposed by G. N. Lewis * who points out that substances like SO_3 and CO_2 behave as acids although they contain no hydrogen. He suggests that an acid is a molecule, radical, or ion which can accept an electron pair from some other atom to complete its stable quota of electrons, usually an octet. A base is a substance which can share this electron pair with an acid. In other words, an acid is an electron "acceptor" and a base is an electron "donor." This definition covers all the acids included in the proton theory of acids and many additional substances also. The fact that this concept is more general makes it less definite in describing the properties of specific acids and bases.

* Luder, The Electronic Theory of Acids and Bases, *Chem. Rev.*, **27**, 547 (1940); Luder and Zuffanti, "Electronic Theory of Acids and Bases," John Wiley & Sons, New York, 1946.

Hydrolysis. It has been shown that a strong acid and a strong base react to give a salt which is completely dissociated. Accordingly, when such a salt is dissolved, it will dissociate to give positive and negative ions, and no change will occur in the hydrogen and hydroxyl ions. However, if the salt is made by neutralization of a weak acid, for example, with a strong base, the negative ions of the salt will react with the hydrogen ions of water to form the weak acid, thus upsetting the equality of free hydroxyl or hydrogen ions. The hydrolysis of sodium acetate to give an alkaline reaction is easily understood by reference to the following reactions:

$$\begin{array}{ccccc} NaC_2H_3O_2 & \rightleftharpoons & Na^+ & + & C_2H_3O_2^- \\ & & + & & + \\ HOH & \rightleftharpoons & OH^- & + & H^+ \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & NaOH & & HC_2H_3O_2 \end{array}$$

The positive sodium ion and the negative hydroxyl ion attract each other, but, since sodium hydroxide is strongly dissociated, there is no decrease in the concentration of hydroxyl ions, but the negative acetate ion and the positive hydrogen ion react to give undissociated molecules of the weak acetic acid. More and more of the water dissociates to supply hydrogen ions for the production of acetic acid molecules. Finally an equilibrium is reached at which there is a definite excess of OH^- ions over H^+ ions. The situation is more simply described by stating that the acetate ions have a greater attraction for protons than the hydroxyl ions. Thus,

$$C_2H_3O_2^- + HOH \rightleftharpoons HC_2H_3O_2 + OH^-$$

Ammonium chloride hydrolyzes in water to give an acid reaction because some of the hydroxyl ions from the water are removed as ammonium hydroxide, leaving an excess of hydrogen ions.

Ferric chloride hydrolyzes to give an acid reaction because ferric hydroxide is a weak base and because the hydroxyl ions are removed by the formation of ferric hydroxide, which is very insoluble.

In general, the reaction between a dissolved salt and the water to give an excess of hydrogen or hydroxyl ions is called *hydrolysis*. The general term for reaction with any solvent is called *solvolysis*.

Any method which gives the effective concentration of hydrogen ions in the hydrolyzed solution permits the calculation of the degree of hydrolysis of a salt. For example, when ammonium chloride ionizes, the ammonium ion reacts with the hydroxyl ion of water, and both are tied up in undissociated ammonium hydroxide, but there is no tendency to produce HCl because it is so strongly dissociated. Each hydroxyl

ion removed leaves an excess of one hydrogen ion, and so the number of excess hydrogen ions is a measure of the number of ammonium chloride molecules which have hydrolyzed.

Example 7. When 1 mole of ammonium chloride is dissolved in 32 liters of water at 25° and allowed to reach equilibrium, a hydrogen electrode in the solution registers 0.605 volt against the normal calomel electrode. Calculate the degree of hydrolysis x.

$$p\mathrm{H} = \frac{0.605 - 0.2802}{0.0591} = 5.48$$

$$\log c_{\mathrm{H}^+} = -5.48 = \bar{6}.52$$

$$c_{\mathrm{H}^+} = 3.3 \times 10^{-6}$$

$$c_{\mathrm{H}^+} = \frac{x \times 1}{v} \quad \text{and} \quad x = 3.3 \times 10^{-6} \times 32 = 1.06 \times 10^{-4}$$

The degree of hydrolysis of a salt may be determined also by means of electrical conductance. When a salt BA hydrolyzes as follows:

$$BA + \mathrm{H_2O} \rightleftharpoons \mathrm{H}A + B\mathrm{OH}$$

the limiting value of its equivalent conductance when hydrolysis is complete is $\Lambda_{HA} + \Lambda_{BOH}$, where Λ_{HA} and Λ_{BOH} denote the equivalent conductances of the acid and base formed. If Λ_s is the equivalent conductance of the unhydrolyzed salt, and Λ_h is the actual conductance of the partially hydrolyzed salt at the same dilution, then the increase in conductance, corresponding to a degree of hydrolysis x, will be $\Lambda_h - \Lambda_s$. If the hydrolysis were complete, the increase in equivalent conductance would be $\Lambda_{HA} + \Lambda_{BOH} - \Lambda_s$; hence,

$$x = \frac{\Lambda_h - \Lambda_s}{\Lambda_{HA} + \Lambda_{BOH} - \Lambda_s} \tag{9}$$

all conductances being measured at the same dilution and at the same temperature. The value of Λ_s, the equivalent conductance of the unhydrolyzed salt, may be found by determining the conductance of the salt in the presence of an excess of one of the products of hydrolysis, and deducting from it the conductance of the substance added. Under these conditions the hydrolysis is rendered negligible.

Example 8. The equivalent conductance of an 0.0108 M solution of aniline hydrochloride is 118.6 reciprocal ohms. When an excess of aniline is added (that is, the solution is saturated with aniline), the equivalent conductance drops to 103.6. The conductance of pure aniline in water is negligible. The equivalent conductance of hydrochloric acid at the same concentration is 411.7. Calculate the degree of hydrolysis x.

$$x = \frac{\Lambda_h - \Lambda_s}{\Lambda_{HA} + \Lambda_{BOH} - \Lambda_s} = \frac{118.6 - 103.6}{411.7 + 0 - 103.6} = 0.047$$

Calculation of Hydrolysis Constants. The hydrolysis of a salt like any chemical reaction reaches a definite equilibrium for which an equilibrium constant can be calculated.

For a salt of a *weak acid* and a strong base, the generalized reaction is

$$BA + H_2O = B^+ + A^- + H_2O = B^+ + OH^- + HA$$

but there is no change in B^+ because both salt and base are fully ionized. The reaction reduces, then, to

$$A^- + H_2O \leftrightarrows OH^- + HA$$

and the equilibrium constant is given by the expression:

$$K = \frac{c_{OH^-} \times c_{HA}}{c_{A^-} \times c_{H_2O}} \tag{10}$$

The concentration of water is regarded as constant because water is present in large excess, and the hydrolysis constant K_h is written

$$K_h = \frac{c_{HA} \times c_{OH^-}}{c_{A^-}} \tag{11}$$

Since the ionization constant of water $K_w = c_{H^+} \times c_{OH^-}$, it follows that

$$c_{OH^-} = \frac{K_w}{c_{H^+}}$$

Also, the dissociation constant of the acid K_a is

$$\frac{c_{H^+} \times c_{A^-}}{c_{HA}} = K_a$$

Substituting these values in equation 11 gives

$$K_h = \frac{K_w}{K_a} \tag{12}$$

The ionization of the salt and the base is practically complete. If the degree of hydrolysis of the salt (that is, the fraction of the ions which react with water) is designated by x and the original concentration of the salt by c_s, then,

$$c_{HA} = xc_s, \quad c_{OH^-} = xc_s, \quad \text{and} \quad c_{A^-} = (1 - x)c_s$$

On substituting these values in equation 11, we have

$$K_h = \frac{K_w}{K_a} = \frac{c_s x^2}{1 - x} \tag{13}$$

and if x the degree of hydrolysis is quite small

$$x = \sqrt{\frac{K_w}{K_a c_s}} \tag{14}$$

Example 9. Calculate at 25° the degree of hydrolysis and the pH of a 0.1 molar solution of potassium cyanide. This is a salt of a strong base and a weak acid. The values of K_{HCN} and K_w are found in the tables.

$$K_h = \frac{K_w}{K_a} = \frac{c_s x^2}{1 - x}$$

$$\frac{1.0 \times 10^{-14}}{7.2 \times 10^{-10}} = \frac{0.1x^2}{1 - x}$$

$$x = 0.0123$$

$$c_{OH^-} = 0.1 \times 0.0123 = 0.00123$$

Assuming that $a_{OH^-} = c_{OH^-}$, we have

$$a_{H^+} \times a_{OH^-} = 10^{14} \text{ and } p\text{H} + p\text{OH} = 7 + 7 = 14$$

Then since

$$p\text{OH} = -\log a_{OH^-} = -\log 0.00123 = -\bar{3}.09 = 2.91$$

$$p\text{H} = 14.00 - 2.91 = 11.09$$

Example 10. Calculate the ion product for water from the fact that a 0.1 molar solution of sodium acetate is 0.0080 per cent hydrolyzed at 25°. The salt as well as the sodium hydroxide formed from its hydrolysis may be considered to be completely ionized. The ionization constant of acetic acid is 1.8×10^{-5}.

$$K_w = K_a \times \frac{c_s x^2}{1 - x} = 1.8 \times 10^{-5} \times \frac{0.1 \times (0.000080)^2}{(1 - 0.000080)}$$

$$= 1.16 \times 10^{-14}$$

Then,

$$c_{H^+} = c_{OH^-} = \sqrt{K_w} = \sqrt{1.16 \times 10^{-14}} = 1.1 \times 10^{-7}$$

Compare this result with that obtained in examples 5 and 6.

A salt of a *weak base* and a strong acid hydrolyzes to give an acid reaction, according to the equation,

$$B^+ + H_2O \leftrightarrows BOH + H^+$$

and, by a reasoning similar to that shown for equation 13, it is found that

$$K_h = \frac{K_w}{K_b} = \frac{c_s x^2}{1 - x} \tag{15}$$

When *both acid and base are weak*, the salt hydrolyzes according to the reaction,

$$H_2O + B^+ + A^- \rightleftarrows BOH + HA$$

and the equilibrium constant is

$$K = \frac{c_{BOH} \times c_{HA}}{c_{B^+} \times c_{A^-} \times c_{H_2O}} \tag{16}$$

Making use of the dissociation constants K_b and K_a for BOH and HA, respectively, we have

$$c_{BOH} = \frac{c_{B^+} \times c_{OH^-}}{K_b}$$

and

$$c_{HA} = \frac{c_{H^+} \times c_{A^-}}{K_a}$$

Then, the equivalent values of c_{BOH} and c_{HA} are substituted into equation 16 and the concentration of water remains practically constant because it is present in such large excess. The hydrolysis constant K_h may be written

$$K_h = \frac{c_{OH^-} \times c_{H^+}}{K_b \times K_a} = \frac{K_w}{K_b K_a} \tag{17}$$

If the weak acid and base both happen to have about the same ionization constant, their concentrations are both approximately equal to the concentration of the hydrolyzed salt, and

$$c_{BOH} = c_{HA} = xc_s$$

Moreover, the concentrations of salt ions are equal to that of the unhydrolyzed salt, and

$$c_{B^+} = c_{A^-} = (1 - x)c_s$$

Substituting these values back into equation 16 gives

$$K_h = \frac{x^2}{(1 - x)^2} \tag{18}$$

When the extent of the hydrolysis is small, equations 17 and 18 can be combined to give

$$x = \sqrt{\frac{K_w}{K_a K_b}} \tag{19}$$

It is to be noted in equation 18 that, in this special case where both base and acid are weak and have about the same ionization constants, there is no term which gives the concentration of the salt, and, accordingly, the degree of hydrolysis is independent of the dilution. In the hydrolyses described by equations 13 and 15, where either the base or the acid is strong, the degree of hydrolysis is greater in low concentration; in fact, when the hydrolysis is slight, it increases inversely as the square of the concentration.

Buffer Solutions. If we turn to Fig. 112 on page 464, we observe that a small drop of acid or base added to water at the neutral point or to pure water will change the *p*H greatly, but that when a solution contains both acetic acid and sodium acetate at a *p*H of about 4 the slope of the line is much less steep, and the addition of either base or acid gives but a slight change in *p*H. A solution which possesses reserve acidity and basicity and, thus, tends to resist changes in *p*H when bases or acids are added is called a *buffer solution*. Buffer solutions usually contain a hydrolyzable salt mixed with the weak base or acid. If a base is added to a buffer solution containing a weak acid HA and one of its salts MA, the alkali is neutralized by the acid; thus:

$$OH^- + HA = H_2O + A^-$$

If an acid is added, the hydrogen ions which it contains react with the anions of the salt to form the undissociated weak acid; thus:

$$H^+ + A^- = HA$$

If the reserve acidity and reserve basicity are to be equal, there must be as many anions A^- to react with added H^+ ions as there are acid molecules HA to react with added OH^- ions. Thus:

$$c_{HA} = c_{A^-}$$

Furthermore, since $c_{H^+} = \dfrac{K_a c_{HA}}{c_{A^-}}$ it follows that

$$c_{H^+} = K_a \tag{20}$$

In other words, the hydrogen-ion concentration is numerically equal to the ionization constant of the acid in a buffer solution which contains equal moles of a weak acid and its salt.

Examples of buffer solutions are given in Table V.

TABLE V

Buffer Solutions

		pH Range
Phthalic acid	+ Potassium acid phthalate	2.2– 3.8
Acetic acid	+ Sodium acetate	3.5– 5.5
Citric acid	+ Disodium phosphate	2.4– 8.0
Boric acid	+ Sodium borate	7.0– 9.1
Disodium phosphate	+ Trisodium phosphate	11.0–12.0

When equivalent weights of the two substances are taken, the pH is near that of the mid-point of the range, and, by altering the ratios of the two, it is possible to change the pH gradually. For example, using normal solutions a ratio of 5 volumes of N citric acid solution to 1 of N disodium phosphate gives a pH of about 3, and a ratio of 1 volume to 5 volumes gives a pH of about 7.

Buffer solutions are important in analytical chemistry, in general laboratory work, and particularly in biochemistry, where it is desired to keep the number of variables to a minimum. Blood, milk, and various animal fluids are highly buffered with bicarbonate ions and carbonic acid, and with many protein systems. The pH of human blood in a normal person is approximately 7.4. Ordinarily variations are less than 0.1 of a pH unit, and an increase or decrease of as much as 0.4 is likely to be fatal.

Different enzymes have certain optimum pH values which must be rather closely maintained. The type of plants growing in a certain locality is largely influenced by the pH of the soil. Forest soil with decaying leaves is likely to be acid, whereas limestone soil will have a higher pH. For proper productivity of crops it is often necessary to add limestone (or sulfur, which changes to sulfuric acid) to give the proper pH to the soil.

Indicators.* Certain weak acids and bases, called indicators, change their color in definite pH ranges. The weak indicator acid competes with strong acid for the added base, and only after the strong acid is neutralized is it affected. When a solution of a base is titrated with an acid, the end point is reached when the amount of acid added is just equivalent to the amount of base present, and the solution should be identical in composition with a solution prepared by dissolving the same weight of salt. However, if the salt is hydrolyzed, it requires an indica-

* A complete discussion of the subject is given by Kolthoff (translation by Rosenblum), "Acid–Base Indicators," Macmillan Co., 1937.

tor which does not change its color at exact neutrality but at the *p*H which is produced by the addition of the salt to the water.

The simplest reaction for an indicator is

$$\underset{\text{(Color } A\text{)}}{HIn} \rightarrow H^+ + \underset{\text{(Color } B\text{)}}{In^-}$$

where the undissociated indicator acid has color *A* and the anion of the acid In^- has a different color *B*. The color is due to resonance, that is, to the motion of electrons in a special type of structure, such, for example, as a system with alternating single and double bonds with suitable groups attached. The vibration period of the electrons in the ion form must be different than that in the undissociated acid. Phenolphthalein, for example, is a weak colorless acid which reacts with sodium hydroxide or other base to give a salt which dissociates to give an anion which is red. Methyl orange, on the other hand, gives an acid which is pink but an anion which is orange.

The *p*H range in which these indicators change color depends on their ionization constant, and they may be selected for use in different ranges as shown in Table VI.

TABLE VI

INDICATORS

Indicator	*p*H Range	Indicator	*p*H Range
Picric acid	0.0–1.3	Brom thymol blue	6.0– 7.6
Thymol blue	1.2–2.8	Phenol red	7.2– 8.8
Brom phenol blue	3.0–4.6	Thymol blue	8.2– 9.8
Methyl orange	3.1–4.4	Phenolphthalein	8.3–10.0
Methyl red	4.4–6.0	Alizarine yellow R	10.1–12.1
Brom cresol purple	5.4–7.0	Nitramine	11.0–13.0

Buffer solutions are widely used as standards in color titrations when it is desired to titrate to a definite *p*H value. They are used also to determine the *p*H of an unknown solution, by comparing the color with a series of colors obtained by adding the indicator to a series of buffer solutions. The *p*H of the solution is the same as that of the particular buffer whose color matches that of the solution. Tables of suitable indicators have been arranged which cover the whole range of *p*H values.

The "neutral color" of an indicator is obtained when there are equal concentrations of the un-ionized acid and the anion forms giving equal

quantities of the two differently colored materials. Under these conditions, since

$$c_{HIn} = c_{In^-}$$

the concentration of hydrogen ions is equal to the dissociation constant of the indicator, thus

$$c_{H^+} = \frac{c_{HIn}}{c_{In^-}} K_{HIn} = K_{HIn} \tag{21}$$

With most indicators it is difficult to detect a sharp color change over a narrow range of pH. Often it is possible to neutralize about 10 per cent of the indicator before a change in color is detectable, and the change does not appear to be complete until about 90 per cent of the indicator is neutralized. Then the visible range of color change gives values of c_{HIn}/c_{In^-} from 0.9/0.1 to 0.1/0.9. This corresponds to a pH range of nearly 2.

The exact ratio of c_{HIn}/c_{In^-} can be determined experimentally by measuring the milliliters of base which must be added to a known amount of indicator to bring about a detectable color change.

Color indicators may be used to show not only when a certain hydrogen-ion concentration is reached but also when a certain ratio of oxidizing to reducing material is reached. In the former case the color change corresponds to a definite voltage of the hydrogen electrode, whereas in the latter it corresponds to a definite voltage of an inert platinum electrode. The loss of color by the reduction of potassium permanganate is well known. The reaction takes place at a definite reduction–oxidation potential. Certain organic compounds such as diphenylbenzidine change color sharply at a given reduction potential and pH. By having a series of these reduction–oxidation indicators and noting which one changes color when placed in a solution, the reduction–oxidation potential of the solution may be readily determined.

Products from some bacterial actions have reducing action and can be tested for, by changing the color of a reduction–oxidation indicator. For example, milk that has been subjected to bacterial action will decolorize methylene blue.

The Solubility Product. The solubility product s is the product of the activities of the ions of an electrolyte in a saturated solution, each activity being raised to its proper exponent. Thus, if $A_nB_m = nA^+ + mB^-$ in a saturated solution,

$$s = a_{A^+}{}^n \times a_{B^-}{}^m \tag{22}$$

Silver chloride may be taken as an illustration. The solubility is 1.1×10^{-5} mole per liter, and, since the dissociation is practically complete,

$c_{Ag^+} = c_{Cl^-} = 1.1 \times 10^{-5}$ gram ion per liter. For the difficultly soluble salts, the solutions are so dilute that the activities are essentially the same as the concentrations, and it is general practice in these cases to use concentrations instead of activities. The equilibrium constant K is

$$K = \frac{c_{Ag^+} \times c_{Cl^-}}{c_{AgCl}}$$

and the solubility product is

$$s = c_{Ag^+} \times c_{Cl^-} = 1.1 \times 10^{-5} \times 1.1 \times 10^{-5} = 1.2 \times 10^{-10}$$

It is not necessary to consider the concentrations or activities of solids in the solubility product because they remain fixed. The activity a of a solute is defined as equal to f/f^0, where the pure solid is taken as the standard state with the fugacity f^0. Then, for the solid, $a = f^0/f^0 = 1$.

Example 11. Calculate the solubility product of silver chromate Ag_2CrO_4 if the solubility is 8×10^{-5} mole per liter.

$$s = c_{Ag^{+2}} \times c_{CrO_4^{--}} = (0.00016)^2(0.00008) = 2 \times 10^{-12}$$

Example 12. The solubility of strontium oxalate at 20° is 0.00054 mole per liter. Calculate the solubility product.

$$s = c_{Sr^{++}} \times c_{C_2O_4^{--}} = (0.00054)(0.00054) = 2.916 \times 10^{-7}$$

How much strontium oxalate will be dissolved in a solution of 0.04 M sodium oxalate? Let x equal the moles of strontium oxalate which dissolve per liter.

$$s = 2.915 \times 10^{-7} = c_{Sr^{++}} \times c_{C_2O_4^{--}} = x(x + 0.04) = x^2 + 0.04x$$

$$x = 7.3 \times 10^{-6} \text{ mole}$$

(x^2 is so small in this example that it may be dropped out in solving this equation.)

A few solubility products are given in Table VII.

TABLE VII

SOLUBILITY PRODUCTS AT 25°

AgCl	1.2×10^{-10}	$Mg(OH)_2$	2×10^{-11}
AgBr	7.7×10^{-13}	CaC_2O_4	2.6×10^{-9}
AgI	0.9×10^{-16}	$CaCO_3$	9.3×10^{-8}
$SrSO_4$	2.8×10^{-7}	PbS	1×10^{-28}
$BaSO_4$	1.1×10^{-10}	MnS	1.4×10^{-15}
$PbSO_4$	1.0×10^{-8}	Ag_2S	1.6×10^{-49}

Example 13. Determine the solubility of silver chloride by means of a silver electrode. The voltage E for the following cell was found to be 0.4550 volt at 25°.

$$\underset{a_{Ag^+} = a_1}{Ag;\ AgCl(sat.),\ KCl(0.1\ m)} \parallel \underset{a_{Ag^+} = a_2}{AgNO_3(0.1\ m);\ Ag}$$

The activity coefficient of 0.1 m $AgNO_3$ is 0.82. Calculating the activity of silver ions in the saturated silver chloride solution at the left:

$$E = 0.4550 = -0.0591 \log \frac{a_1}{a_2} = -0.0591 \log \frac{a_1}{0.82 \times 0.1}$$

$$a_1 = 1.67 \times 10^{-9}$$

The activity coefficient of 0.1 m KCl is 0.76, and it is not appreciably changed by the very small amount of silver chloride dissolved. Then,

$$a_{Ag^+} \times a_{Cl^-} = (1.67 \times 10^{-9}) \times (0.76 \times 0.1) = 1.27 \times 10^{-10}$$

When silver chloride is dissolved in pure water, the concentrations of silver and chloride ions are equal. Moreover, the solution is so dilute that the activities are the same as the concentrations. Then,

$$\text{Solubility} = \sqrt{c_{Ag^+} \times c_{Cl^-}} \cong \sqrt{a_{Ag^+} \times a_{Cl^-}} = \sqrt{1.27 \times 10^{-10}}$$

$$= 1.13 \times 10^{-5} \text{ mole of silver chloride per 1000 g of water}$$

Classification of Strong Electrolytes. Thus far this chapter has dealt mostly with weak electrolytes, which exist largely in the form of undissociated or un-ionized molecules. They include many organic acids and bases and a few inorganic compounds. The strong electrolytes, which include almost all salts, the mineral acids like hydrochloric and sulfuric, and the alkali hydroxides, will now be discussed.

Several properties of these strong electrolytes have been studied in earlier chapters—the activities of electrolytes and the dissociated ions as determined by electromotive-force measurements, the abnormal lowering of the freezing point, and the change of equivalent conductance with dilution. The distinction between strong and weak electrolytes is not sharp, and there are, of course, many electrolytes which are intermediate in their behavior.

Dilute solutions are used for studying the properties of strong electrolytes because the properties of the ions are additive at infinite dilution. For example, the heats of formation of the ions in dilute solution can be used for calculating the heats of reaction of electrolytes. Again, the absorption spectra of strong electrolytes in dilute solutions are usually characteristic of the individual ions as, for example, in the case of the permanganates of sodium, potassium, ammonium, zinc, magnesium, and hydrogen, all of which give the same absorption spectrum.

In addition to the distinction between weak electrolytes and strong electrolytes, another subclassification of strong electrolytes based on valences is useful. In the 1–1 electrolytes the positive and negative ions both have a valence of one as in NaCl, HNO_3 and KOH; whereas in the 2–2 electrolytes both positive and negative ions have a valence of two as in $ZnSO_4$ and $CuSO_4$. The first term refers to the positive ions, the second to the negative ions; thus, H_2SO_4 and K_2CO_3 are 1–2 electrolytes, $Ba(OH)_2$ and $Pb(NO_3)_2$ are 2–1, $Al(OH)_3$ is 3–1, and $Al_2(SO_4)_3$ is a 3–2 electrolyte.

The total number of ions ν is important in determining the factor by which the freezing-point depression or other property must be multiplied in very dilute solutions. For NaCl, $\nu = 2$; for $CuSO_4$, $\nu = 2$; for $BaCl_2$, $\nu = 3$; for $K_3Fe(CN)_6$, $\nu = 4$; and so on. In more concentrated solutions the multiplication factors are smaller than these numbers, as shown on page 249, because the effect of the attraction between ions becomes greater at the higher concentrations. On account of the greater attraction between ions with more than one electric charge, the solutes containing high valence ions cause greater deviations from the values obtained at infinite dilution than do the 1–1 electrolytes—a theory which is fully verified by experiment. The charges on the ions can be treated most successfully in terms of the *ionic strength*, a term which was first used by G. N. Lewis.* In calculating the ionic strength μ of a strong electrolyte, the concentration of each ion (in gram ions per 1000 g of solvent) is multiplied by the square of its valence, and all these quantities are added together and divided by 2.†

Example 14. Calculate the ionic strength of the following solutions of electrolytes.

For 0.01 m NaCl, $$\mu = \frac{0.01 \times 1^2 + 0.01 \times 1^2}{2} = 0.01$$

For 0.01 m $CuSO_4$, $$\mu = \frac{0.01 \times 2^2 + 0.01 \times 2^2}{2} = 0.04$$

For 0.01 m H_2SO_4, $$\mu = \frac{0.01 \times 1^2 + 0.01 \times 1^2 + 0.01 \times 2^2}{2} = 0.03$$

Several properties of electrolytes at a given molality depend not on the specific electrolyte but merely on the ionic strength.

For example, an equal number of moles of sodium chloride, potassium nitrate, and lithium perchlorate all have the same effect on the

* Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, page 373.

† Sometimes concentrations on a volume basis rather than a weight basis are used, particularly in applications of the Debye–Hückel theory.

solubility of thallous bromide. Since they are all 1–1 electrolytes, they will have the same ionic strength at the same concentration. Moreover, since the ionic strength of copper sulfate is four times that of a 1–1 electrolyte at the same concentration, the effect of copper sulfate on the solubility, or other properties which involve interionic attraction, will be four times as great as the effect of sodium chloride at the same molality.

Again, for strong electrolytes in dilute solution the ionic strength determines to a large extent the influence of concentration on the departure from the behavior of ideal solutions. The quantitative deviations are shown in Table VIII.

TABLE VIII

Influence of Ionic Strength on Behavior of Strong Electrolytes

Electrolyte	Molality	Ionic Strength	Molal Freezing-Point Depression	$i = \frac{\Delta T_f/m}{1.860}$	$\frac{i}{\nu}$
KCl	0.01	0.01	3.610	1.943	0.97
$AgNO_3$	0.01	0.01	3.60	1.94	0.97
$CuSO_4$	0.01	0.04	2.703	1.45	0.73
$ZnSO_4$	0.01	0.04	2.80	1.51	0.76
K_2SO_4	0.01	0.03	5.198	2.80	0.93
$LaCl_3$	0.01	0.06	8.0	4.3	1.07
$K_3Fe(CN)_6$	0.01	0.06	6.966	3.75	0.94
$K_4Fe(CN)_6$	0.01	0.10	6.8	3.66	0.73
KCl	0.05	0.05	3.50	1.88	0.94
K_2SO_4	0.0167	0.05	5.02	2.70	0.90
$CuSO_4$	0.0125	0.05	2.66	1.43	0.72
$LaCl_3$	0.0083	0.05	6.6	3.55	0.89
$K_3Fe(CN)_6$	0.0083	0.05	6.75	3.63	0.91
$K_4Fe(CN)_6$	0.0050	0.05	7.1	3.8	0.76

The ratio i was shown on page 248 to be the ratio of the freezing-point lowering of a given solute to the freezing-point lowering of an ideal nonelectrolyte. Thus, $i = (\Delta T_f/m)/1.860$. As the solution approaches infinite dilution, i approaches ν, where ν is the number of ions (1, 2, or 3, etc.) into which the electrolyte dissociates, as shown in Fig. 67 on page 249.

The ratio i/ν then approaches 1 at infinite dilution, and it becomes less than unity in more concentrated solutions, as the charged ions collide

more frequently and cause a departure from the behavior of an ideal solution. The point to be observed in the table is that, for salts of a given valence type, the magnitude of this ratio i/ν depends largely on the ionic strength. At a given concentration all 1–1 electrolytes have a nearly the same value of i/ν, regardless of the chemical nature of the salt such as KCl, NaBr or $AgNO_3$, and 1–2 electrolytes and 2–2 electrolytes have other definite values, depending on the ionic strength.

The ionic strength, then, is more fundamental than the chemical composition of the electrolyte in predicting how the freezing-point depression or other related osmotic properties of strong electrolytes will differ from the properties at infinite dilution. These relations apply also to weak electrolytes, but, then, the much greater effect of partial ionization makes them relatively unimportant. For weak electrolytes i/ν may be used to calculate the degree of dissociation. But for strong electrolytes i/ν differs from unity owing in part to interionic attraction, and it does not give the degree of dissociation.

Interionic Attraction. The behavior of strong electrolytes in moderate concentrations can be understood in a qualitative way by realizing that oppositely charged ions attract each other and cause deviations from the behavior of ideal solutions, just as to a lesser degree the attraction between molecules in a gas causes deviations from the behavior of an ideal gas. The quantitative aspects of the theory have been developed by Debye and Hückel, as is shown later. The positive and negative ions are so far apart in very dilute solutions that they exert no attractions on each other, and the molal freezing-point depression or other osmotic property is just twice as much for a 1–1 electrolyte like potassium chloride as it is for a nonelectrolyte like sugar. According to one view, the addition of nonvolatile ions to water decreases the rate at which the water molecules can leave any surface and thus reduces the vapor pressure of the water. However, when the solution is at all concentrated, the interionic attraction tends to pull the ions inward away from a surface, thus making the water-blocking effect less per ion. The magnitude of this interionic attraction depends not only on the concentration but also on the valence type; a divalent ion with its two charges exerts a greater interionic attraction than a univalent ion. These two influences find quantitative expression in the ionic strength, as described in the preceding section.

It might be thought that there is no essential difference between these partially attracted ions of the interionic attraction theory and the undissociated molecules of the Arrhenius theory. For weak electrolytes the Arrhenius theory is adequate, but for strong electrolytes it offers no explanation of the important effect of valence type and ionic

strength. Moreover the experimental evidence, such as the ionic nature of the crystal lattice, supports the view that most strong electrolytes are largely dissociated into ions.

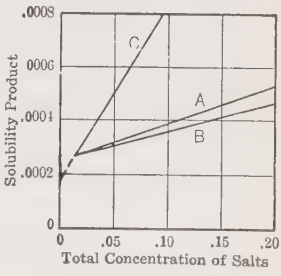
The interionic attraction theory explains not only the influence of concentration on the osmotic properties of strong electrolytes, but also the effect of electrolytes on the solubility of salts. The effect of a common ion in decreasing the solubility of a difficultly soluble salt was treated under the discussion of the solubility product, but this relation fails to hold accurately if the solution contains a high concentration of electrolytes. It does not apply to highly soluble salts, nor does it account for the *increase* in solubility produced by the addition of other electrolytes which do not have a common ion. The solubility of thallous chloride in various salt solutions * comprised one of the first investigations to show the influence of an excess of electrolytes on solubility. In pure water thallous chloride dissolves to the extent of about 0.016 mole per liter; when potassium chloride is added, the solubility is decreased; but, when potassium nitrate is added, the solubility is increased—one tenth of a mole per liter raising the solubility to 0.019 mole per liter. Potassium nitrate contains no ion common with thallous chloride, and it might be expected to have no effect. It will be remembered that in a saturated solution there is a dynamic equilibrium with molecules or ions going into solution from the crystal and returning to the crystal. The rate of escape of ions from the crystal is not influenced by the addition of electrolytes to the solution, but the number of collisions on the crystal from solution is decreased by the addition of ionized substances, because each positive ion is drawn to the solution by a mass of negative ions and each negative ion by a mass of positive ions. A greater total concentration is required in the presence of extra ions to give an *effective* concentration sufficient to maintain equilibrium conditions with the crystal. Consequently, the analytically determined solubility is increased. It is fair to imagine that potassium chloride itself exerts (1) an effect of interionic attraction which tends to increase the solubility of thallous chloride, and (2) a common-ion effect which tends to decrease the solubility.

The increase in solubility due to the addition of any electrolyte leads to a corresponding increase in the solubility product as more electrolyte is added. In **Fig. 116** are shown the results with the 1–1 electrolyte, thallous chloride, and the 2–2 electrolyte, calcium sulfate. The deviations in the latter are much greater than in the former as is to be expected on account of the higher ionic strength at a given molality and the greater interionic attraction of the divalent calcium and sulfate ions.

* Bray and Winninghoff, *J. Am. Chem. Soc.*, **33**, 1663 (1911).

If equation 22 for the solubility product applied rigorously, all the lines would be horizontal.

The decrease in the measured activity of ions, produced by the addition of other electrolytes, and the departure from the ideal behavior as the solution of strong electrolytes becomes more concentrated can now be offered as an explanation of the need for activity coefficients in understanding the electromotive force of solutions. The potential of an electrode immersed in a solution of its ions is determined in part by the frequency with which the ions collide with the surface of the electrode. When this collision frequency is decreased, the potential will become less positive, if the electrode exchanges electrons with positive ions in contact with it, and less negative, if it exchanges electrons with negative ions. When a given potential is registered by an electrode in a very dilute solution of its ions, the potential should change by RT/nF log 10 or $0.059/n$ volt at 25° for a tenfold increase in concentration. However, the change will be less than this, because the interionic attraction and the correction for effective concentration will be greater in the more concentrated solution. This correction for effective concentration is determined by experiment and designated as the activity coefficient.



A. TlCl with KNO_3
B. TlCl with KCl
C. $CaSO_4$ with $CaCl_2$

FIG. 116. Influence of salts on solubility products of TlCl and $CaSO_4$.

The interionic attraction theory in the quantitative form developed by Debye and Hückel makes it possible to calculate these activity coefficients in dilute solutions.

The Debye–Hückel Theory. The interionic attraction theory has already been employed to explain in a qualitative way various phenomena involving ions. It was shown on page 509 that the mutual attraction between positive and negative ions at ordinary concentrations leads to a smaller decrease in vapor pressure than is to be expected on the assumption of complete separation at infinite dilution. This effect leads also to similar decreases in the freezing-point depression and other colligative properties. Abnormalities in solubilities and solubility products and single-electrode potentials were interpreted also on the basis of this theory as was the change in electrical conductances of strong electrolytes with concentration.

When the dissociation of strong electrolytes is complete, the properties mentioned in the preceding paragraph can be treated quantita-

tively with the help of the Debye–Hückel theory.* When the dissociation is incomplete, however (as is true in the case of sulfuric acid, cadmium chloride, calcium iodate, and several inorganic salts and most organic compounds), the theory does not describe the behavior completely because electrolytic dissociation is still important. The Debye–Hückel theory has been remarkably successful when applied to most strong electrolytes in dilute solution.

The mathematical development of the Debye–Hückel theory is given in the appendix on page 680. It is based on the work required to separate the ions in the process of dilution. The attractive or repulsive forces are governed by Coulomb's law of charged bodies and depend on the magnitude of the ionic charges and the distance between ions as given by the expression e_1e_2/Dr^2, where e_1 and e_2 represent the charges, D the dielectric constant of the solvent, and r the average distance between ions. In very dilute solutions r becomes so great that this attractive force approaches zero, and the simple laws of complete dissociation are adequate. Debye and Hückel derived the following expression, which holds for strong electrolytes in dilute solution,

$$-\ln \gamma_i = \frac{e^3 z_i^2}{(DkT)^{3/2}} \sqrt{\frac{2\pi N\mu}{1000}} \tag{23}$$

where γ_i = activity coefficient of ion species i (page 470)
z_i = charge on ion species i
e = charge of an electron = 4.803×10^{-10} electrostatic unit
D = dielectric constant of the solution = 78.56 for water at 298° K
N = Avogadro's number = 6.023×10^{23}
k = gas constant per molecule = $R/N = 1.3805 \times 10^{-16}$ erg per degree
μ = ionic strength = $\frac{1}{2}(c_1z_1^2 + c_2z_2^2 + c_3z_3^2 + \cdots)$, the summation being taken over all the ions in the solution
c_i = concentration of ion species i in moles per liter

Equation 23 shows that in dilute solution the activity coefficient of an ion depends only on its valence, the ionic strength, the dielectric constant of the medium, and the temperature. Hence, all univalent ions, for example (both positive and negative), in the same solution will have the same activity coefficients.

If we introduce the mean activity coefficient γ of the electrolyte

* Debye and Hückel, *Physik. Z.*, **24**, 185, 305 (1923); Noyes, *J. Am. Chem. Soc.*, **46**, 1080, 1098 (1924); **47**, 2122 (1925).

(page 470) and put in numerical values for water at 25°, equation 23 becomes, for an electrolyte composed of just two kinds of ions,

$$-\log \gamma = 0.509 z_1 z_2 \sqrt{\mu} \qquad (24)$$

The numerical constant will be different for solvents other than water and for temperatures other than 25°. In this equation z_1 and z_2 are the number of electric charges on the ions (without regard to the sign).

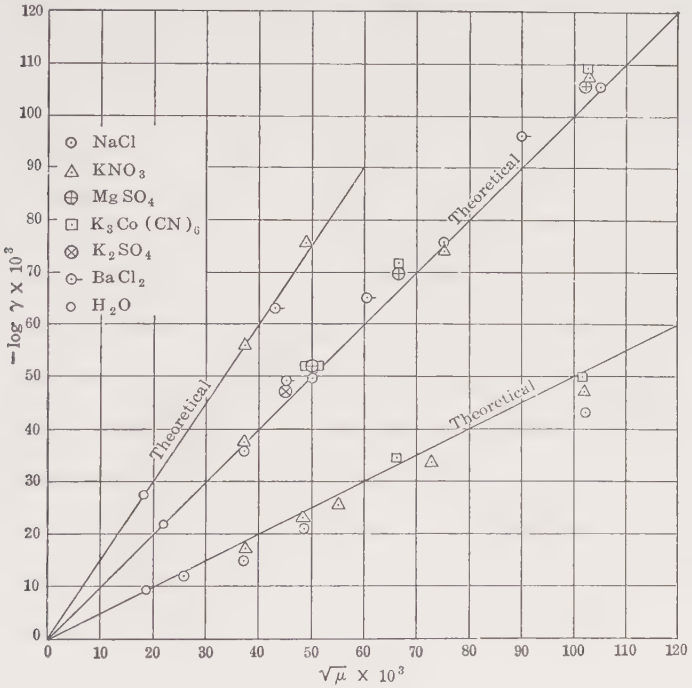


Fig. 117. Influence of salts of different valence type on activity coefficient.

A test of this equation is shown in **Fig. 117.** Brönsted and LaMer * determined the solubility of certain complex cobalt amines in salt solutions of various ionic-charge types and compared the solubility with the solubility in pure water, thus obtaining values of the activity coefficients γ. In Fig. 117, $-\log \gamma$ is plotted against $\sqrt{\mu}$. The lowest line corresponds to a 1–1 cobalt compound where $z_1 z_2$ is 1, and the slope is seen to be 0.5. The ionic strength of the solution rather than the specific nature of the added salt determines the value of γ. The next line corresponds to a cobalt salt of the 1–2 type where $z_1 z_2$ has a value of 2, and the slope is $2 \times 0.5 = 1$. The steepest line in Fig. 117 cor-

* Brönsted and LaMer, *J. Am. Chem. Soc.*, **46**, 555 (1924).

responds to a 1–3 compound where $z_1 z_2$ is 3, and the slope is 1.5. This equation gives a theoretical justification for the ionic strength μ which Lewis found, empirically, to be of considerable importance in the study of electrolytes. It emphasizes the fact that *in dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength, regardless of the specific electrolytes added.*

Concentrated Solutions. Thus far the discussion has been concerned only with behavior of the solute and the mutual electric attraction of its ions. In concentrated solutions and in certain solvents other factors are involved. In actual practice the properties of the *solution* are measured rather than the properties of the isolated solute, and interaction with the solvent or with other ions must be considered.

There is ample evidence that many solutes combine with the water to form hydrates. The term *solvates* is more general, applying as it does to any solvent. This evidence includes color changes, shifts of absorption bands, deviations from Beers' law of light absorption, abnormal osmotic properties, abnormal conductance values, transport of solvent along with solute in electrolysis, transference numbers, and so on.

The formation of ion–hydrates or ion–solvates is easily interpreted as being due to an ion–dipole attraction. The ions have a definite positive or negative charge, and the molecules of those solvents, such as water, ammonia, and alcohol, which produce electrolytic dissociation, have large dipole moments. There is a definite force of attraction between two such units. Liquids of small dipole moment such as benzene and carbon tetrachloride fail to dissolve the alkali halides and other electrolytes which might be expected to ionize. In fact, it is the reaction between solute and solvent, the ion–dipole interaction, which provides energy sufficient to separate the solid into its ions and put them into solution.

Another result of this interaction between ion and solvent is a profound change in the nature of the solvent in concentrated solutions, as, for example, in water containing high concentrations of dissolved salts. Nonelectrolytes such as ether and gases are thrown out of a saturated solution when sodium chloride is added in large quantities. Again, in the extraction of salts from water by shaking with ether or other immiscible solvent, the extraction is greatly facilitated by the addition of large quantities of electrolytes which interact with the dipoles of the water and change the properties of the water so as to decrease its solvent effect. Sometimes the salt interacts with the new solute and increases the solubility.

Another phenomenon which brings out the abnormal behavior of water in concentrated solutions is the molal depression of the freezing

point. The molal depression at infinite dilution for 1–1 electrolytes is 3.7° and for 2–1 electrolytes is 5.56. When the concentration is increased, the molal depression decreases, as is to be expected from Fig. 67 on page 249, but, when the concentration approaches half-molal, the molal depression starts to *increase;* in $MgCl_2$ and $CaCl_2$ it is larger at 1-molal than it is at infinite dilution—and in 2-molal solution it is over 9°. The increases are but slight in electrolytes which do not form hydrates, and the large increases in $MgCl_2$ and $CaCl_2$ are probably due to the fact that these salts form hexahydrates, $CaCl_2 \cdot 6H_2O$, for example, so that at the high concentrations much of the water is tied up with the solutes, reducing the amount of normal solvent water and producing a higher *effective* concentration and, hence, an abnormally greater depression of the freezing point.

Complex Ions. Electrolytes other than 1–1 electrolytes can ionize, theoretically, in steps as in the case of sulfuric acid:

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

$$HSO_4^- \rightarrow H^+ + SO_4^{--}$$

The tendency to form HSO_4^- ion is greater in concentrated solutions, because in dilute solutions the HSO_4^- ion will ionize further, as indicated by the second reaction.

Many examples of complex ions are known in which two or more ions or groups combine to form larger ions which have distinctly different properties. Thus, for example, when sodium cyanide is added to silver nitrate, AgCN is precipitated, but, when an excess of cyanide is added, the precipitate dissolves, owing to the formation of a complex ion, according to the reaction:

$$2CN^- + Ag^+ \rightleftarrows Ag(CN)_2^-$$

This complex ion $Ag(CN)_2^-$ is quite stable and has properties quite different from either CN^- or Ag^+. It is negatively charged and moves to the anode in electrolytes carrying silver in the direction opposite to that in which Ag^+ ion travels.

These complex ions can be explained in many cases as due to an interaction between an ion and a molecule with a high dipole moment, as, for example, the deep blue ion $Cu(NH_3)_2^{++}$ which is produced when ammonia or ammonium hydroxide is added to a solution of a cupric salt.

Summary of Concentration Ranges. It may be concluded from what has been said in this chapter that aqueous solutions of electrolytes may be classified roughly into four different groups, depending on the concentration.

In exceedingly dilute solutions (less than 0.0001 M for strong electrolytes and much less for weak electrolytes), the solute is completely dissociated, in agreement with either the Arrhenius or the interionic attraction theory.

In dilute solutions (0.0001 to 0.01 M) the Arrhenius theory is satisfactory only for weak electrolytes such as acetic acid, but even here interionic attraction is a factor. The Arrhenius theory does not apply to the strong electrolytes, but the interionic-attraction theory is necessary for strong electrolytes. Again, however, partial dissociation is a factor, even in some inorganic electrolytes which might be expected to be largely dissociated.

In solutions of moderate concentration (0.01 M to 1 M) the properties of strong electrolytes are affected both by interionic attraction and by the presence of un-ionized molecules. The mere fact that one can smell hydrochloric acid molecules from a 1 M solution of HCl proves that some undissociated molecules exist in the solution. Exact theoretical calculations cannot yet be made in this region.

In concentrated solutions (greater than 1 M) the character of the solvent is markedly changed by the presence of the solute, and the situation is very complicated. Hydration or solvation of the solute and depolymerization of the solvent may be factors.

These classifications are to be taken only as rough approximations, and they vary greatly for different electrolytes. Apparently, some salts, such as mercuric chloride and cadmium chloride, are only very slightly dissociated, even in dilute solution.

In nonaqueous solutions with low dielectric constants the interpretation is more difficult, and, in general, the solutions must be more dilute than the aqueous solutions before the theoretical equations can be applied.

Theories of Conductance.* Although theories of conductance do not properly belong in a chapter on ionic equilibria, the following brief discussion has been postponed until after the presentation of the interionic attraction theory. The earlier attempts to explain the phenomena

* Additional material on this subject may be found in the following references. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., New York, 1946; Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1943; Kraus, The Present State of the Problem of Electrolytic Solutions, *J. Chem. Education*, **12**, 567 (1935); MacInnes, The Interionic Attraction Theory of Electrolytes, *Science*, **86**, 23 (1937); "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939, Chapters 18 and 19; Fuoss, Properties of Electrolytic Solutions, *Chem. Rev.*, **17**, 27 (1935); Davidson, Recent Advances in the Electrochemistry of Non-Aqueous Solutions, *J. Chem. Education*, **14**, 218 (1937).

of the electrical conductance of strong electrolytes were handicapped by an overemphasis of the Arrhenius theory and a lack of data concerning nonaqueous solutions. Rapid advances following the Debye–Hückel theory of interionic attraction, broader investigations with different solvents, including those of low dielectric constant, and improved experimental techniques now permit a fairly quantitative understanding of the conductance behavior of dilute aqueous solutions and extremely dilute nonaqueous solutions. Moreover, the causes of deviations in the more concentrated solutions are now known, at least in part. The aqueous solutions and the solutions of high dielectric constant are still the simplest to interpret. It may be remembered that the conductance depends on both the number of ions and the velocity of the ions. In some strong electrolytes the ionization is so complete that the changes in equivalent conductance are concerned with the mobility of the ions.

According to the present theory, each ion in a solution is surrounded by an ionic atmosphere of central symmetry, resulting from the combined effect of Coulomb forces between the charged ions and the thermal agitation. When an external potential is applied, the electrical force overcomes the ordinary frictional resistance to the motion of the ions, and they move toward the electrode of opposite charge. This motion, however, sets up two retarding forces. The first, known as the relaxation force, is the result of the movement of the ion from the center of its atmosphere under the influence of the applied potential. Since the atmosphere requires a finite time for its formation, a portion of the atmosphere will lag behind its normal position, producing a dissymmetry in the direction of motion and causing the ion to suffer a reduced mobility.

The second retarding force arises from an electroosmotic motion of the solvent in the direction opposite to that of the ion in question. The effect of each of these forces can be expressed in ordinary conductance units, as pointed out by Debye and Hückel, and Onsager,* thus,

$$\Lambda = \Lambda_0 - \Lambda_{\mathrm{I}} - \Lambda_{\mathrm{II}} = \Lambda_0 - a\sqrt{c}\,\Lambda_0 - b\sqrt{c} \qquad (25)$$

where Λ_0 is the conductance at infinite dilution, Λ_{I} is the relaxation force and Λ_{II} the electrophoretic force, c is the concentration and a and b are theoretical constants derived from a mathematical treatment of this ionic atmosphere. For a 1–1 strong electrolyte in water at 25°, equation 25 is

$$\Lambda = \Lambda_0 - (59.8 + 0.227\Lambda_0)\sqrt{c} \qquad (26)$$

* Onsager, *Physik. Z.*, **28**, 277 (1927).

In an alternating field each ion in solution will acquire a periodic reaction. If the frequency is increased to a point where the period of oscillation of the ion becomes comparable with the time of relaxation, the dissymmetry in the ionic atmosphere will decrease, the effect of the electric force of relaxation will diminish, and the equivalent conductance will increase. Also, by the application of very high voltages, the ion may be forced to move fast enough to escape completely from its atmosphere, so that both retarding forces disappear, and the equivalent conductance approaches its limiting value at infinite dilution. Debye, Falkenhagen, Wien, and Onsager have all made theoretical studies of frequency and field strength, and the results are in general accord with the experimental facts.

Fuoss has developed an equation which gives straight lines when the function Λ_0/Λ (corrected for interionic attraction) is plotted against a function of the concentration and the square of the activity coefficient. It applies in dilute solutions to all electrolytes in various solvents. In solvents of low dielectric constant (below 10) it applies only to the extremely dilute solutions, and a minimum is observed in the curve at higher concentrations. This behavior is due to the formation of a complex between a molecule and one of the ions. Such combinations are less likely to occur in solutions of high dielectric constant.

In benzene and other solvents of extremely low dielectric constant there is a combination of ions and molecules into still larger aggregates, as shown, for example, in the abnormally small depression of the freezing point. The abnormalities are greatest in the case of small ions with large dipole moments.

In general, the properties of an electrolytic solution depend on the solvating power and the dielectric constant of the solvent, and on the size, configuration, and space distribution of the ions. In water which has a dielectric constant of 78 and a marked tendency to combine with ions, there is no detectable difference in the ionization of potassium chloride, potassium bromide, and potassium iodide, but there is a marked difference in liquid ammonia which has a dielectric constant of 22 and a lesser tendency to solvate. At $-34°$ in ammonia, the dissociation constants for potassium iodide and chloride are, respectively, 0.0042 and 0.00087. Those electrolytes with the largest ions are the most highly dissociated in a given solvent.

The generalizations discussed in this section apply only to dilute solutions. In concentrated solutions the phenomena are too complicated to describe with mathematical formulas yet devised. Finally, it should be pointed out that electrical conduction is an irreversible process and that it is distinct from freezing-point lowering and other reversible processes which are of interest in thermodynamics.

REFERENCES

GLASSTONE, "Introduction to Electrochemistry," D. Van Nostrand Co., New York, 1942.

MACINNES, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939.

HARNED and OWEN, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1943.

HAMMETT, "Solutions of Electrolytes," McGraw-Hill Book Co., New York, 1936.

DOLE, "Experimental and Theoretical Electrochemistry," McGraw-Hill Book Co., New York, 1935.

GLASSTONE, "Text-book of Physical Chemistry," D. Van Nostrand Co., New York, 1946.

PROBLEMS

1. At 25° the equivalent conductance of propionic acid at infinite dilution is 385.6 ohms, and the ionization constant is 1.34×10^{-5}. Calculate the equivalent conductance of a 0.05 N solution of propionic acid at 25°. *Ans.* 6.32 ohm^{-1}.

2. At 40° the ionization constant of ammonium hydroxide is 2.0×10^{-5}. (*a*) What is the OH^- ion activity in a 0.1 M solution? (*b*) What is the OH^- ion activity of a solution 0.1 M with respect to ammonium hydroxide which is also 0.1 M with respect to ammonium chloride, if the latter is assumed to be completely ionized?

Ans. (*a*) 1.4×10^{-3}. (*b*) 2.0×10^{-5}.

3. The ionization constant of ammonium hydroxide is 1.4×10^{-5} at 0° and 2×10^{-5} at 40°. What is the average heat of ionization of ammonium hydroxide in this range of temperature? *Ans.* 1516 cal.

4. Gas containing 20% O_2, 78% N_2, 0.3% CO_2, and the rest noble gases is confined above distilled water at room temperature. What is the pH of the water? What is the concentration of the H^+ ions?

$$CO_2\ (aq) = CO_2\ (g) \qquad K_p = \frac{p_{mm}}{N} = 1.25 \times 10^6$$

$$CO_2\ (aq) + H_2O = H_2CO_3 \qquad K_c = \frac{c_{H_2CO_3}}{c_{CO_2}} = 6.8 \times 10^{-3}$$

$$H_2CO_3 = H^+ + HCO_3^- \qquad K_i = 3 \times 10^{-7}$$

Ans. pH = 6.2.

5. The electromotive force of the cell,

$$Pt,\ (H_2\ (1\ atm);\ C_6H_5NH_2 \cdot HCl\ (0.03125\ m)) \,||\, \text{normal calomel electrode}$$

is 0.464 volt at 25°. Calculate the per cent hydrolysis of the aniline hydrochloride.

Ans. 2.4 per cent.

6. It can be shown that for an aqueous solution of a salt of a weak base and strong acid the hydrogen-ion concentration is given by

$$c_{H^+} = \sqrt{\frac{K_w}{K_b} c_s}$$

where c_s = concentration in mole per liter
K_w = ionization constant of water
K_b = ionization constant of base

Pyridinium perchlorate is such a salt. If $K_b = 1.6 \times 10^{-9}$, what is the pH of a 0.0001 molar solution? *Ans.* pH = 4.60.

7. The specific conductance at 25° of a saturated solution of barium sulfate was 4.58×10^{-6} reciprocal ohm, and that of the water used was 1.52×10^{-6}. The equivalent conductance at infinite dilution of barium sulfate is 143. What is the solubility of $BaSO_4$ at 25° in (*a*) gram equivalents per liter, (*b*) moles per liter, and (*c*) grams per liter?

Ans. (*a*) 2.14×10^{-5} equivalent per liter. (*b*) 1.07×10^{-5} mole per liter. (*c*) 2.50×10^{-3} g per liter.

8. The solubility product of silver bromide at 18° is 4.1×10^{-13}. Calculate:

(*a*) The solubility of silver bromide in pure water.

(*b*) The solubility of silver bromide in 0.1 molar NaBr.

Ans. (*a*) 6.40×10^{-7} mole per liter. (*b*) 4.1×10^{-12} mole per liter.

9. At 25° the potential of the cell,

$$\text{Ag, AgI; KI (1 } M\text{) } || \text{ AgNO}_3 \text{ (0.001 } M\text{); Ag}$$

is 0.72 volt. In a molal solution of KI the activity coefficient of I^- ion is 0.65, and in 0.001 M $AgNO_3$ the activity coefficient of Ag^+ ion is 0.98. (*a*) What is the solubility product of AgI? (*b*) If no salt effect is assumed, what would be the solubility of AgI in pure water?

Ans. (*a*) 4.2×10^{-16}. (*b*) 2.1×10^{-8} mole per 1000 g H_2O.

10. Alanine dissociates in the following manner in acid solutions:

$$\overset{+}{\text{N}}\text{H}_3\text{CH(CH}_3\text{)—COOH} = \text{H}^+ + \overset{+}{\text{N}}\text{H}_3\text{—CH(CH}_3\text{)COO}^-$$

and

$$K = \frac{c_{\text{H}^+} \times c_{\text{R}^{+-}}}{c_{\text{R}^+}} = 0.0040$$

In a solution whose pH is 3, what is the per cent dissociation of the alanine?

Ans. 79.9 per cent.

---

11. How many hydrogen ions are there in 1 ml of an 0.1 molar solution of an acid which has a dissociation constant of (*a*) 1×10^{-3}; (*b*) 1×10^{-10}; (*c*) 6×10^{-23}?

12. Alanine is an amino acid which dissociates into both H^+ and OH^- ions. At 25° the dissociation constant for the dissociation into anions and hydrogen ions is 1.99×10^{-10}. The apparent dissociation constant for the dissociation into cations and hydroxyl ions is 5.25×10^{-12}. At what pH would you expect the osmotic pressure of an alanine solution to be a minimum?

13. (*a*) What is the hydrogen-ion concentration of a 0.5 molar solution of NH_4Br at 25° after hydrolysis? The ionization constant of NH_4OH is 1.8×10^{-5}. (*b*) What is the pH?

14. (*a*) Calculate and record in tabular form the degree of hydrolysis x of a 1.0 N solution of a salt of a weak acid and a strong base if the ionization constant for the acid is 10^{-4}, 10^{-6}, and 10^{-10}.

(*b*) Repeat the calculation of (*a*) for a 0.01 N solution.

15. Calculate the pH at 25° of a buffer solution containing 50 ml of 0.2 M potassium hydrogen phthalate and 45.45 ml of 0.2 M NaOH solution all diluted to 200 ml. The dissociation constant for the second hydrogen of phthalic acid at 25° is 3.1×10^{-6}.

16. It is customary to express $-\log K$ as pK. For the dissociation of 5-ethyl 5-hexyl barbituric acid at 25° in aqueous solution pK is 7.79. What is the standard free-energy change (ΔF^0) for the reaction $HA\ (aq) = H^+ + A^-$?

17. The specific conductance of a saturated solution of thallous bromide at 20° is 2.158×10^{-4} and the specific conductance of water at the same temperature is 0.044×10^{-6} reciprocal ohms. The equivalent conductance at infinite dilution is 138.3. Calculate the solubility of thallous bromide in grams per liter.

18. The solubility of strontium oxalate at 20° is 0.00054 mole per liter. What is the solubility product? How much strontium oxalate would dissolve in a solution having an oxalate-ion concentration of 0.04 gram ion per liter?

19. What is the ionic strength of 0.02 M solutions of each of the following substances: (*a*) LiCl, (*b*) K_2SO_4, (*c*) $MgSO_4$, (*d*) Na_3PO_4, (*e*) $K_4Fe(CN)_6$?

20. The free-energy formation of AgCl (*s*) is −26,187 cal at 25°. From the standard electrode potentials calculate the solubility product of AgCl and compare it with the experimental value of 1.56×10^{-10}.

---

21. Five grams of lactic acid is diluted with water to 1 liter. How many gram ions of hydrogen are present in the solution? The dissociation constant of lactic acid is 1.36×10^{-4} at 25°.

22. For benzoic acid at 25° the ionization constant is 7.3×10^{-5}. Calculate the pH of a 0.001 molar solution of benzoic acid at 25°.

23. An 0.1 M solution of iodic acid HIO_3 is 72.5 per cent dissociated. Calculate the freezing point of this solution, assuming that the degree of dissociation does not change with the temperature.

24. (*a*) Derive a general equation for calculating the degree of dissociation for an electrolyte which dissociates into three ions, as, for example, oxalic acid ($(COOH)_2 = 2H^+ + C_2O_4^{--}$). (*b*) Give the approximate formula, assuming that α is very small. (*c*) Calculate K in terms of the Λ conductances.

25. The ionization constants at 25° for acetic acid, lactic acid, and bromoacetic acid are 1.8×10^{-5}, 1.4×10^{-4}, and 1.4×10^{-3}, respectively. (*a*) Calculate α for a 0.01 molar solution of each of these acids by the approximate method (assuming $1 - \alpha = 1$) and (*b*) by the exact method.

26. Leucylglycine is an amino acid which dissociates into both H^+ and OH^- ions. At 25° the dissociation constant for the dissociation into anions and hydrogen ions is 1.51×10^{-8}. The apparent dissociation constant for the dissociation into cations and hydroxyl ions is 3.02×10^{-11}. Calculate the pH at which the degree of dissociation into hydrogen ions and hydroxyl ions is the same.

27. The hydrolysis constant of aniline hydrochloride is 2.25×10^{-5}, and the ionization constant of aniline is 4.2×10^{-10} at 25°. Calculate the concentration of the H^+ and OH^- ions in water.

28. The specific conductance of a saturated solution of AgCl in water was found to be 2.279×10^{-6} mho. The specific conductance of the water used was 1.16×10^{-6} mho. Using the table of ionic conductances, page 417, calculate:

(*a*) The solubility of AgCl in grams per liter.

(*b*) The solubility product of AgCl.

29. A solution of sodium chloride has an ionic strength of 0.24. (*a*) What is its concentration? (*b*) What concentration of Na_2SO_4 would have the same ionic strength? (*c*) What concentration of $MgSO_4$?

30. What is the ionic strength of a 0.4 M solution of: (*a*) $MnCl_2$; (*b*) $MnSO_4$; (*c*) $AuCl_3$; (*d*) $Fe_2(SO_4)_3$?

31. $2Ag + CO_3^{--} = Ag_2CO_3 + 2e$ $\quad E^0 = -0.50$ at 25°

$Ag^+ + \frac{1}{2}H_2 = H^+ + Ag$ $\quad E^0 = 0.799$ at 25°

What is the solubility of Ag_2CO_3 in moles per liter at this temperature?

---

32. The first ionization constant of H_2S in water is 9.1×10^{-8}; the second is 1.2×10^{-15}. The solubility of H_2S in water is 3.4 g per liter. How many grams of Pb $(NO_3)_2$ added to 1 liter of saturated H_2S solution will just start precipitation of PbS?

33. Show that if K_a and K_b do not differ by more than a hundredfold the H^+ concentration and the OH^- concentration will be *practically* equal in the hydrolyzed salt.

34. Proteins probably exist in solution as dipole ions or ("zwitterions"), that is, ions having both negative and positive charges. The effect of the addition of acids or bases to such substances may be seen from the equations:

$$\overset{+}{N}H_3RCOO^- + H^+ = \overset{+}{N}H_3RCOOH$$

$$\overset{+}{N}H_3RCOO^- + OH^- = NH_3OHRCOO^-$$

Show that the actual ionization constant as an acid is equal to the hydrolysis constant of the basic part, and vice versa.

35. Calculate the free energy of neutralization of a mole of strong acid by a mole of strong base in a dilute aqueous solution at 25°, K_w being 10^{-14}.

36. In the case of the hydrolysis of a salt of a strong base and weak acid show that

$$c_{H^+} = \sqrt{\frac{K_a K_w}{c}}$$

where K_a = ionization constant of the acid, K_w = ionization constant of water, and c = concentration of salt in moles per liter. Derive the expression for the pH of such a solution. How will an increase in concentration of salt affect the pH of the solution? Test this by determining the pH of 0.1 N and of 1 N sodium isobutyrate at 25° ($K_a = 0.98 \times 10^{-5}$).

37. Given an amphoteric electrolyte XOH capable of dissociating according to both of the equations:

$$XOH = XO^- + H^+$$

$$XOH = X^+ + OH^-$$

If the basic dissociation constant is K_b and the acidic dissociation constant K_a, derive the expression for the hydrogen-ion concentration in a solution of this electrolyte as a function of the concentration of the un-ionized substance.

38. A solution of 9.94 g of Na_2SO_4 in 1000 g of water produces the same lowering of the vapor pressure as an 0.169 molal solution of urea. What is the activity coefficient of Na_2SO_4 in this solution? Urea does not dissociate.

CHAPTER XVIII

COLLOIDS

Definitions. In the course of his investigations on diffusion in solutions, Thomas Graham * drew a distinction between crystalline solutes and certain amorphous solutes such as starch, albumin, and caramel which diffuse much more slowly. To this latter type of substance he gave the name *colloid* (from the Greek "glue forming"). These colloids give solutions which have very low osmotic pressures and freezing points which are nearly the same as those of the pure solvent. The term colloid, as now used, applies not so much to a class of material as to a state of subdivision.

If the particles of a substance are reduced in size until the dimensions become submicroscopic and distributed throughout a second substance, the resulting system is called a *disperse system.* The particles are called *dispersoids,* and the suspending liquid, gas, or solid is called the *dispersing medium.* The characteristic properties of disperse systems are attributable to the enormous surface of the dispersed phase. If a cube of any substance 1 cm on an edge, having a total surface of 6 sq cm, is cut in half in the three directions, there will be 8 cubes having edges of 0.5 cm, and the surface will be $8 \times 6 \times 0.5^2$ or 12 sq cm. If cut into 1000 cubes 1 mm on an edge, the total surface will be 60 sq cm. If the cubes are 1μ † on an edge, the surface area will be increased to 60,000 sq cm, or 6 sq m. If the cubes are 0.001μ on an edge, there will be 10^{21} cubes, and the area will be 6000 sq m or $1\frac{1}{2}$ acres. Particles as small as this contain only a few molecules because the diameter of simple molecules is of the order of 1A, and 1A = 10^{-8} cm or $10^{-4}\mu$. It is obvious that surface effects which are undetected on material having an area of 6 sq cm may become very pronounced when the material is dispersed to give a total surface of several square meters.

One of the most important results of this large surface is the adsorption of ions and other materials by the particles. This adsorption may lead to the formation of electric charges on the particles which prevent them from collecting into large aggregates.

* Graham, *Trans. Roy. Soc. (London),* **151,** 183 (1861).

† The symbol μ refers to a micron which is 10^{-3} mm or 10^{-4} cm.

If the particles are large, they can be seen with the naked eye, and they have essentially the properties of ordinary material, whereas, if they are extremely small, of the order of molecular dimensions, they are indistinguishable from true solutions. Between these two regions is the colloidal state, in which the particles are small enough to have great surface area but large enough so that the solution is not strictly homogeneous and the presence of discrete particles can be detected with the ultramicroscope. The size of the dispersed particles determines whether or not a system is to be considered as colloidal. It is arbitrarily considered that particles with diameters between 0.001μ and 1μ (10^{-7} and 10^{-4} cm) are colloids, although there is no sharp distinction at these extremes. Particles larger than 1μ may be regarded as ordinary matter, and particles less than 0.001μ are usually regarded as constituting true solutions. Dust particles may have a diameter of 10^{-4} cm, and hemoglobin or egg albumin or certain particles of colloidal gold have diameters of about 10^{-7} cm.

Colloids are conveniently classed as *lyophylic* colloids, when the dispersion medium exerts a dissolving or attractive influence on the dispersed phase, and as *lyophobic* colloids, when there is very little attraction between the particles and the liquid in which they are suspended.

Preparation of Colloids. Colloids may be produced by *dispersion methods* in which relatively coarse material is divided into fine particles of colloidal dimensions. Liquids may be dispersed in gases by directing a stream of gas across a constantly renewed liquid surface as in an "atomizer." A liquid may sometimes be dispersed in a second liquid, in which it is insoluble, by merely shaking the two liquids together. A colloidal *emulsion* consists of small droplets of the first liquid 10^{-7} -- 10^{-4} cm in diameter suspended throughout the second liquid. An emulsifying agent, such as soap, is usually added to aid in the formation of the emulsion. Liquids or solids can be effectively dispersed in liquids by means of the *colloid mill*.* Large drops or coarse particles are suspended in water or other liquid and exposed to a powerful shearing force in the mill by passing the material between two accurately machined disks which rotate in opposite directions at a very high velocity while nearly but not quite touching each other.

Colloids are more often prepared by *condensation methods* in which the molecules or small aggregates are gathered together into larger aggregates. This procedure is thermodynamically spontaneous for it involves a decrease in surface area and a decrease in free energy of the

* Travis, "Mechanochemistry and the Colloid Mill," Chemical Catalog Co. New York, 1928.

system. Condensation methods may be illustrated by the formation of precipitates in solution or by the cooling of water vapor to give a fog. Metals may be produced in the colloidal state by being vaporized with an electric arc and condensed under water.

This simple method, used first by Bredig, is shown in **Fig. 118.** An arc is struck by pulling the two electrodes slightly apart, using for example a 110-volt circuit, at 5 to 10 amperes. Somewhat better results are obtained with a housing around the arc which keeps the liquid from contacting the ends of the wires. Colloids of silver, platinum, gold, and other metals can be prepared, using the proper electrodes. Red colloidal gold solution can be prepared containing over 10 mg of gold per 100 ml of water.

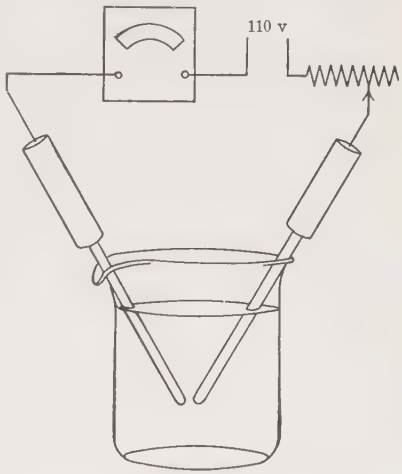


FIG. 118. Preparation of colloids by the arc method.

By means of a high-frequency arc, Svedberg and his coworkers have succeeded in preparing colloids of most of the metals, including those of the alkalies. Ether, free from water and oxygen, may be employed as the dispersion medium.

Lyophobic colloids are often produced by precipitation reactions if the concentration of electrolytes is kept low. If there is a high concentration of ions, the colloidal particles are likely to form large particles and settle out as described later.

The following reactions in which electrolytes are not produced illustrate the formation of colloids by direct chemical precipitation:

$$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$$

$$2H_2S + SO_2 = 3S + 2H_2O$$

$$Ni(CO)_4 = Ni + 4CO$$

In the first reaction, if arsenous chloride is used in place of the arsenous acid, hydrochloric acid will be produced in the reaction instead of water, and the arsenous sulfide will be partly coagulated by the ions produced.

Even when electrolytes are produced, it is possible to obtain the precipitate in the colloidal state if the solutions are dilute. The forma-

tion of colloidal ferric oxide by the reaction of ferric chloride with an excess of water, the production of colloidal gold by reduction of auric chloride with reducing agents such as tannic acid or formaldehyde, and precipitation of colloidal barium sulfate or silver chloride or silicic acid are examples of this common method of preparing colloids. In order to preserve the colloids, it is sometimes necessary to remove the electrolytes by techniques which are described in the following sections.

Material in solution may sometimes be thrown out in the colloidal state by mixing the solution with a second solvent in which the material is less soluble. For example, sulfur dissolved in alcohol is obtained as a white milky colloid solution when poured into an excess of water.

The classical methods for preparing colloids which have just been described refer chiefly to the lyophobic colloids. The lyophylic colloids are, perhaps, of more general importance, particularly in the fields of biology and industrial chemistry. Resins are natural or artificial mixtures of organic nature formed by such reactions. They dissolve in organic solvents in the early stages of their formation and separate out in films when the solvent is evaporated. They are usually amorphous and sometimes possess a glassy nature. Rubber, the asphalts, the cellulose derivatives, and the synthetic and natural resins are formed in reactions of this general type. Natural resins are excreted from plants; shellac, from animal organisms.

The production of lyophylic colloids often involves a process of solution or dispersion in which the solvent overcomes the attractive force between molecules which is due to dipole-dipole interaction. Nitrocellulose for example is dissolved by acetone or by a mixture of ether and alcohol giving collodion, and the colloidal properties of the system are retained after the solvent has been evaporated. Rubber dissolved in carbon tetrachloride, starch in aqueous solutions of zinc chloride for use in dry batteries, casein taken up in dilute acid or alkali solutions are all examples of lyophylic colloids. The nonaqueous colloidal systems are becoming increasingly important with the extensive use of lacquers such, for example, as a polymer of phthalic anhydride and glycerine dissolved in an organic solvent such as acetone or dioxane.

The polymerization reactions in which molecules react chemically to form larger aggregates are particularly important. Several of these have been studied in detail,* including the polymerization of the hydroxy acids. The ethylene derivatives polymerize according to the following reaction:

$$n(CH_2 = CHX) \rightarrow (CH_2 - CHX)_n$$

* Carothers, *Chem. Rev.*, **18**, 367 (1931); Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936); **61**, 3334 (1939).

where X is a group such as C_6H_5, OH, Cl or OCH_3. The polystyrenes produced from $H_2C = CHC_6H_5$ constitute a specific example. Some of these polymerization reactions can be studied as they proceed by the determination of increasing molecular weights of the particles or by measurement of the viscosity.

The separation of proteins and other colloids into different fractions can be brought about by changing the solvent, the salt concentration, and the temperature and *p*H.*

Purification of Colloids. The difference between the diffusion rates of electrolytes and colloids permits a separation. If a solution containing both crystalline material and colloids is separated from pure water by a colloidal membrane, such as parchment, the crystalloids will pass through the membrane, and the colloids will be left behind. This process was termed *dialysis* by Graham, and the apparatus employed to effect such a separation is called a *dialyzer*. When, for example, a solution of sodium silicate is added to an excess of hydrochloric acid and placed in a dialyzer, the resulting sodium chloride and the hydrochloric acid diffuse away, leaving colloidal silicic acid.

Various natural and artificial membranes may be used for dialysis; Visking sausage casings of cellulose acetate are widely used, or sacks of thin collodion may easily be prepared. These membranes contain small pores which provide continuous channels for the solution, through which dissolved molecules and ions can diffuse, but through which the large colloid particles cannot diffuse. Dialysis may be regarded as a process of fractional diffusion of solutes and colloids; it is not to be confused with osmosis in which nothing but solvent can pass through the semi-permeable membrane. The rate of dialysis depends on many factors—the area of the dialyzer, the size of the pores, the temperature, the electric charges, and the relative concentration of solution on the two sides of the membrane. In practical work, fresh water is passed around the dialyzing sack to expedite the separation. Sometimes the solution is heated.

In the process of electrodialysis, the dialyzing chamber is placed between two electrodes and the ions migrate from the colloidal solution to the electrode which is opposite in sign.

Many colloids are prepared under conditions where an excess of ions is present, and they are rendered more stable by dialysis. It is possible, however, to remove too many ions and cause coagulation.

In the process of *ultrafiltration* the liquid medium as well as the material in true solution is removed from the colloidal material. Pressure is applied to the solution in a strong cylinder so as to force the liquid

* Cohn, *et al.*, *J. Am. Chem. Soc.*, **62**, 3386, 3396 (1940); **68**, 459 (1946).

through the very small holes of a special membrane. A tank of compressed gas offers a convenient source of pressure. Filter papers may be used for ultrafiltration if they are first impregnated with solutions of collodion in acetic acid. Graded filters of different effective pore size can be made by changing the concentration of the acid.* Ultrafiltration is a complex process, involving electric attraction and adsorption by the filter as well as the ordinary process of mechanical separation.

Ultrafilters are useful in removing impurities from sols, and they find extensive application in bacteriology. Bacteria can generally be removed from solutions by ultrafilters, but certain diseases such as the common cold are connected with viruses which pass through fine ultrafilters.

Optical Behavior. When a narrow beam of sunlight is admitted into a darkened room, the dust particles in its path are rendered visible by the scattering of the light at the surface of the particles. If the air of the room is free from dust, the beam of light cannot be seen when viewed from the side, and the space is said to be "optically void."

The luminosity of the path of a beam of light is known as the *Tyndall effect* and may be considered as an indication of the presence of suspended particles, provided the luminosity is not caused by fluorescence. Almost all colloid solutions exhibit this phenomenon when a powerful beam of light is passed through them, thus proving the presence of discrete particles in the solutions.

Great advances in colloid chemistry came with the invention of the ultramicroscope in 1903 by Siedentopf and Zsigmondy. With this instrument the motions of the colloid particles became visible. In an ultramicroscope a powerful beam of light is brought to a focus within the colloidal solution, and this image is viewed through a standard microscope, the axis of which is at right angles to the path of the beam. When examined in this way, a colloid solution usually appears to be swarming with tiny bright particles moving rapidly in a dark field, whereas a true solution if properly prepared appears optically void.

It is necessary to view the particles by reflected light rather than by transmitted light because the colloidal particles are smaller than the wave length of visible light. The intensity of the light rather than the magnifying power of the microscope is the limiting factor in detecting the smallest colloid particles with the ultramicroscope. It is possible to extend the lower limit of detection by using shorter wave lengths, that is, ultraviolet light, with quartz lenses and photographic plates. It should be emphasized that the apparent size of the bright image bears no relation to the size of the particle. It is possible, however, to count

* Ferry, Ultrafilter Membranes and Ultrafiltration, *Chem. Rev.*, **18**, 373–455 (1937).

the number of particles in a given volume. By means of a chemical analysis, the mass of colloid per unit of volume can be determined, and from this the average mass of each particle can be calculated.

Example 1. In the field of an ultramicroscope, 20 particles of colloidal mercury were observed. This field, approximately 0.02 mm wide, comprised a volume of 1×10^{-9} ml. A liter of this colloidal mercury solution was stirred rapidly with a gold stirrer until all the mercury had amalgamated with the stirrer and removed from solution. The increase in weight of the stirrer was 8 mg. Assuming that the particles of mercury were spherical and that they had a density of 13.5, calculate the average radius of the colloidal particles.

$$20 \times \frac{1 \times 10^{3}}{1 \times 10^{-9}} = 2 \times 10^{13} \text{ particles per liter}$$

$$0.008 = 2 \times 10^{13} \times \tfrac{4}{3} \times 3.14 \times r^{3} \times 13.5$$

$$r = 1.9 \times 10^{-6} = 190 \text{ A}$$

These small colloid particles can be seen with the ultramicroscope only if their refractive index differs from that of the medium in which they are suspended. With metallic colloids this difference is large, and excellent definition is obtained, making possible the detection of particles as small as 0.004μ or 40 A in diameter. The marked difference in the behavior of lyophobic and lyophylic colloids is evident also in the observation of them through an ultramicroscope. The lyophylic colloids are partly combined with the solvent, and, accordingly, it is much more difficult to see lyophylic colloids than lyophobic colloids in the ultramicroscope, even if they are fairly large.

A new instrument, the electron microscope, is now available for examining much smaller particles. The principle of the electron microscope depends on the fact that a beam of electrons under a constant voltage has the properties of a beam of light. At the voltages used the wave length corresponds to 0.05 A, and it is clear why particles which are much smaller than the wave length of visible light 4000 to 8000 A may still be observed with the electron microscope. Practical difficulties limit the utilization of the full theoretical resolving power of the electron microscope, but photographs with good detail can be obtained with a magnification of more than 100,000 times.

The electron microscope is provided with a series of electrostatic and electromagnetic fields which focus the electron beam just as glass lenses focus ordinary light. The voltage and current must be closely controlled. The specimen to be studied is placed on a very thin collodion film and a focused beam of electrons is passed through. Where the material is denser, more of the electrons are scattered, but, where the ma-

terial is thin, the electrons continue on their course and are focused on a fluorescent screen or a photographic plate.

With the electron microscope several viruses such as tobacco mosaic virus have been pictured, and they are found to be rod-shaped in agreement with indirect measurements based on diffusion. Also, the size and shape characteristic of different paint pigments and specially effective abrasives have been established. Moreover, structural features in the simplest bacteria have been brought out. A picture of bacteriophage which grows on bacteria as taken by Dr. T. F. Anderson is shown in **Fig. 119.***

FIG. 119. Electron microscope picture of bacteriophage.

Kinetic Behavior. Very small particles suspended in a liquid can be seen under the microscope to be in a state of ceaseless erratic motion. Colloid particles as seen in the ultramicroscope undergo this motion, but larger particles which can be seen with an ordinary lens, such as an aqueous suspension of gamboge, also exhibit a slow movement. This phenomenon, which had frequently been observed, was first properly interpreted in 1827 by the English botanist, Robert Brown, while examining a suspension of pollen grains. It is commonly known as *Brownian motion.* Brown stated that "the movements arose neither from currents in the fluid nor from its gradual evaporation, but belonged to the particle itself."

It is now known that the movement is caused by the actual bombardment of the particles by the molecules of the suspending medium. It constitutes a visual confirmation of the random kinetic motion which had been assumed for the molecules of a gas (or liquid or solid) at any temperature above absolute zero.

This kinetic behavior is responsible for many of the important phenomena of colloids. It is used for separating different colloids and for determining their sizes and shapes. The particle sizes can be determined not only by direct photographing with an electron microscope or by counting with an ultramicroscope as already described, but in several indirect ways including diffusions and sedimentations under gravity or

* A shadowgraph technique was used in which gold atoms are evaporated onto the specimen at an oblique angle. T. F. Anderson, Morphological and Chemical Relations in Viruses and Bacteriophage, Cold Spring Harbor *Symp. Quant. Biol.* **11,** 1–13 (1947).

centrifugal force. Measurements of osmotic pressure may be used also. These phenomena will now be discussed in more detail.

Diffusion. It is to be expected that material will diffuse from a region of higher concentration. The rate of this diffusion has been studied quantitatively, and it has a number of applications in the study of colloids. The diffusion constant or specific diffusion rate D is defined as the number of moles which diffuse across a unit area in unit time under a concentration gradient of unity. It can be shown (appendix, page 688) that

$$D = \frac{RT}{Nf} \tag{1}$$

where f is the frictional force opposing a particle which is moving with a velocity of 1 cm per second, N is Avogadro's number, and R is the gas constant.

According to Stokes's law this force is given by equation 2,

$$f = 6\pi\eta r \tag{2}$$

where r is the radius of the spherical particle and η is the coefficient of viscosity of the surrounding medium. This formula was derived for particles which are large compared to the solvent molecules, and, strictly speaking, it applies only to spherical molecules. Combining equations 1 and 2 gives

$$D = \frac{RT}{N6\pi\eta r} \tag{3}$$

This is a useful equation from which the diffusion rate can be determined from the radius of the particle and the viscosity of the medium; or the size of the particle can be calculated from the rate of the diffusion of the colloids. One of the applications of this equation is the calculation of the Avogadro number N.

The intimate relationship between Brownian movement and diffusion was shown for the first time by Einstein.* The actual movements of individual colloidal particles are seen to be complex and erratic, just as the motions of molecules in a gas had been imagined.

In **Fig. 120** each circle represents the position of an individual colloid particle at intervals of 30 seconds as it is seen under the ultramicroscope while it moves along a path from A to B and on to P and Q. The dotted lines give the displacements along the x axis. Then Δx is the difference between two successive displacements. For example, in going from A to B, Δx is obtained by subtracting the second dotted line from the top

* Einstein, *Ann. Physik*, [4] **17**, 549 (1905); **19**, 371 (1906).

one, and $\Delta x/\Delta t$ is equal to this distance divided by the 30-second time interval Δt. Of course, there will be movement also along the z axis at right angles to the x–y plane, but the displacements along any one axis are sufficient to calculate the diffusion rate or particle size.

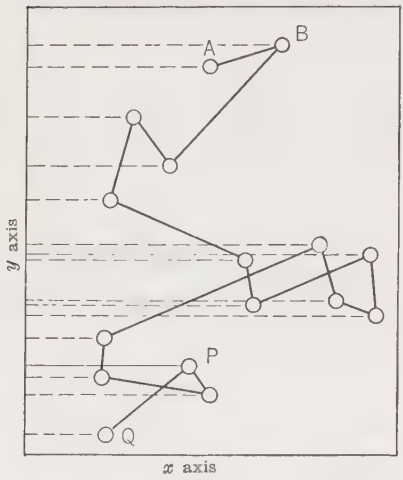


FIG. 120. Movement of a colloidal particle from A to Q with intermediate positions shown every 30 seconds.

The mean value of the square of the difference in the x displacements $(\overline{\Delta x})^2$ is related to the diffusion constant by Einstein's relation as follows,

$$\frac{(\overline{\Delta x})^2}{\Delta t} = 2D \qquad (4)$$

Then substituting in equation 3 gives

$$(\overline{\Delta x})^2 = \frac{RT}{N}\frac{\Delta t}{3\pi\eta r} \qquad (5)$$

Using suspensions of certain gums in water, Perrin measured with a microscope and scale the displacements of a single particle at successive time intervals. He calculated the radius r by counting the particles obtained from a given weight of material, assuming that the particles were spherical. In this way he obtained an average value of 6.8×10^{23} for the Avogadro number N.

More accurate values for the Avogadro number have been obtained by Millikan and Fletcher,* employing a minute drop of oil as the suspended particle. In the gaseous state, where the intermolecular distances are greater than in the liquid state, not only are the collisions less frequent, but also the mean free paths are appreciably longer. These conditions are favorable to the study of the Brownian movement and offer an opportunity for the determination of the Avogadro constant with a high degree of accuracy. These measurements taken under conditions which are more favorable for the study of Brownian motion lead to a value of 6.03×10^{23}.

This value is in perfect agreement with the value of the Avogadro number given on page 626, a fact which strengthens both the kinetic theory of gases and the assumption that these comparatively large particles behave as individual molecules in a gas.

* Fletcher, *Phys. Rev.*, **4**, 453 (1914).

The diffusion method has been used for determining the sizes of particles under different conditions. The rate of diffusion can be measured by a number of different methods—by direct chemical analysis of samples at different distances after definite time intervals, or by methods depending on the Tyndall effect or the absorption or refraction of light. Perhaps the simplest general method involves photographing a scale with fine divisions behind a boundary between a solution and the solvent. The distortion of the photograph of the scale due to differing refractive indices locates the boundary. With a series of photographs taken at successive time intervals it is possible to calculate the rate at which the solute diffuses and changes the refractive index. Great care must be exercised in eliminating mechanical vibrations and thermal inequalities.*

Although equation 3 was derived only for spherical particles, it can be used in connection with certain other formulas if the shape factor occurs in both formulas in such a way as to cancel out. More recently the determinations of the diffusion constants has become important because they can be combined with measurements of sedimentation or viscosity to give the molecular weights of dissolved proteins or carbohydrates even when the shape of the colloid particle is unknown.†

Viscosity. Whereas the viscosity of a liquid is not markedly changed by the addition of a small amount of a lyophobic colloid such as colloidal gold in water, the viscosity of lyophylic colloidal solutions may become very great. The viscosity of high polymers, such as nitrocellulose, has long been used as a criterion for certain industrial operations, and now progress is being made in correlating viscosity with the size and shapes of the colloidal particles.

The particles may be spheres, rods, disks, or threads, and valuable information concerning the shape and the molecular weight can be obtained from measurements of viscosity.

In the case of a dilute suspension of hard spheres Einstein showed that the viscosity η is given by

$$\eta = \eta_0(1 + 2.5\phi)$$

where η_0 is the viscosity of the solvent and ϕ is the total volume of the spheres contained in 1 ml of the suspension. This expression can be written

$$\frac{\dfrac{\eta}{\eta_0} - 1}{\phi} = \frac{\eta_{sp}}{\phi} = 2.5$$

* Williams and Cady, Molecular Diffusion in Solution, *Chem. Rev.*, **14**, 171 (1935).

† Svedberg and Pedersen, "The Ultracentrifuge," Oxford University Press, Oxford, 1940.

where the term $\eta/\eta_0 - 1$ is defined as the *specific viscosity*. A more significant quantity is the *intrinsic viscosity* $[\eta]$ defined as the limit of η_{sp}/c as c is extrapolated to zero concentration—that is, infinite dilution. The term c is defined as the number of grams of polymer in 100 cc of solution.

According to a modification of Staudinger's equation *,

$$[\eta] = kM^a \tag{6}$$

where M is the molecular weight of the polymer and k and a are constants which depend on the type of polymer, the solvent, and the temperature. The constant a varies from 0.5 for tightly curled polymers to 2 for long straight molecules. When the molecular weight is known from osmotic measurements or other considerations, valuable information regarding the length and shape of the polymer may be obtained from these determinations of intrinsic viscosity.

Osmotic Pressure. The osmotic pressure or the lowering of the freezing point by colloids is exceedingly small, but it is nevertheless real. If the molar weight of a colloid is regarded as 6.02×10^{23} times the weight of a single particle, it is clear that the molecular weights of colloids must be enormous. Obviously, the molecular weight must be very large because the diameter of atoms is of the order of 1 A, whereas the diameter of colloid particles ranges from 10 A to 10,000 A. However, there is some doubt as to the propriety of referring to the molecular weight of colloids, particularly in view of the fact that the individual particles vary greatly in size. It is better to speak of molar particle weight rather than molar weight of a colloid, and it must be realized that such a term refers to an average particle weight multiplied by Avogadro's constant.

The ordinary methods for determining molecular weights in solution are beset with difficulties when applied to colloid systems because it is almost impossible to wash out all the ions, and each ion is just as effective as a colloid particle in lowering the vapor pressure or the freezing point, or in creating an osmotic pressure. Furthermore, the effect to be measured is very small. It may be remembered that 6×10^{23} molecules dissolved in 1000 g of water will lower the freezing point 1.86°, and, if ten thousand of these units are combined into one colloid particle, the freezing-point lowering will be only 0.000186°. A mere trace of electrolyte left behind will produce an effect greater than this.

A few satisfactory measurements have been made using collodion membranes and measuring the apparent osmotic pressure of concentrated

* Mark, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, New York, 1940, pages 258–293.

solutions under conditions where ions do not affect the pressure. The holes in the collodion membrane are large enough to let the ions pass, but they block the passage of the large colloid particles. An excess of electrolyte is added to the colloid solution and to the solvent on the two sides of the membrane. The ions diffuse through and reach equilibrium, so that the measured osmotic pressure is due only to the colloids. By rigorous control of the amount of electrolyte present, Sorensen found a molecular weight of 34,000 for egg albumin, and Adair * obtained 67,000 for hemoglobin.

Example 2. A solution of 1 g of a nitrocellulose in a liter of acetone has an osmotic pressure of 0.56×10^{-3} atm at 27°. Assuming that the solution is ideal, calculate the molar particle weight of the nitrocellulose.

$$Pv = \frac{gRT}{M}$$

$$M = \frac{gRT}{Pv} = \frac{1 \times 0.08205 \times 300.1}{0.56 \times 10^{-3} \times 1} = 44{,}000$$

Sedimentation Equilibrium. The distribution of colloid particles under a given force such as gravity is directly related to diffusion and osmotic pressure. When a solution is allowed to stand, a state of equilibrium is finally reached when sedimentation and diffusion balance each other, that is, when in a given interval of time the amount of material which falls in the downward direction through a unit area is the same as that which diffuses upward on account of the greater concentration at the lower level. The most familiar example of a sedimentation equilibrium is the atmosphere of the earth.

The quantitative formula for the concentration as a function of height makes possible the determination of the molecular weight of a solute, provided the solution is dilute enough for the ordinary laws of dilute solutions to hold. It should be noted particularly that the equation contains only well-defined and measurable quantities, and its validity is independent of the shape of the particles. The formula for sedimentation equilibrium can be derived by thermodynamics for a colloidal solution containing particles of uniform size, using the following symbols:

n = number of particles per milliliter, that is, the concentration
x = the distance of the particle from the bottom of the vessel
g = acceleration of gravity
S = density of the particle
S_0 = density of the liquid
v = volume of the particle

* Adair, *Proc. Roy. Soc.* (*London*), **A 109**, 292 (1925).

Two forces are acting: the force of gravity (or other force) tends to pull the particles to the bottom of the vessel, thus increasing the concentration; and the kinetic force causes the particles to diffuse away from the region of higher concentration at the bottom.

The force of gravity pulling one particle downward is $v(S - S_0)g$, allowing for the buoyancy of the liquid.

The change in free energy ΔF for the transfer of a mole of particles from one concentration to another is given on page 245 by the equation:

$$\ln \frac{n_2}{n_1} = \frac{\Delta F}{RT} \tag{7}$$

At equilibrium the decrease in free energy must be equal to the work w done by a mole of the particles (N particles) against the force of gravity acting through the distance $x_1 - x_2$. Then,

$$\ln \frac{n_2}{n_1} = \frac{w}{RT} = \frac{Nv(S - S_0)g(x_1 - x_2)}{RT} \tag{8}$$

The same equation can be derived from considerations of diffusion rates. The values of n_2 and n_1 may be obtained by counting the number of particles in a given field with a traveling microscope.

Example 3. The number of particles in a given volume of a solution of colloidal gold which had come to equilibrium in the earth's gravitational field was found to be 392 at one level and 196 at a level 0.10 mm higher. The temperature was 20°, and the diameter of the particles was 0.066μ. The specific gravity of gold is 19.3, and that of the colloidal solution may be assumed to be 1. What is the value of Avogadro's number as calculated from these data?

$$2.303 \log \frac{392}{196} = \frac{N \times \frac{4\pi}{3}(3.3 \times 10^{-6})^3(19.3 - 1.0)(981)(0.01)}{8.31 \times 10^7 \times 293}$$

$$N = 6.2 \times 10^{23}$$

The Ultracentrifuge. The sedimentation due to the force of gravity is so small that it can be used only for the largest particles. The sedimentation force may be increased enormously, however, by using centrifugal force, and it is thus possible to determine particle size of the smallest particles—even down to large molecules in true solution. Svedberg has contributed greatly to this field.

In the centrifuge the acceleration of gravity is replaced by centrifugal force $\omega^2 x$, where ω is the angular rotational velocity, $2\pi \times$ the number of revolutions per second, and x is the distance from the center of rotation.

Then integrating $\omega^2 x\, dx$ and substituting for $g(x_1 - x_2)$ in equation 8, we have

$$\ln \frac{n_2}{n_1} = \frac{\frac{1}{2}\omega^2(x_1^2 - x_2^2)Nv(S - S_0)}{RT} \tag{9}$$

An additional advantage of the ultracentrifuge is that the sedimentation force may be controlled.

Sedimentation equilibrium measurements using equation 9 require much time and effort, and a different technique is often used in which the velocity of sedimentation rather than the concentration of particles at equilibrium is measured.

In operating the velocity ultracentrifuge, the solution is placed in a small cell inserted in the rotor. The cell has transparent windows, and in the chamber which encloses the rotor there are corresponding windows with electromagnetic shutters. The cell is partially filled with the colloid solution, and to the remainder of the cell is added a suitable solution which gives a line of demarkation at the edge of the colloid solution. By directing a beam of light through the windows one can note the effects of the centrifugal force as this line owing to differences in refractive index or light absorption moves outward. A diagram showing the principle of the Svedberg ultracentrifuge is given in **Fig. 121.** Photographic

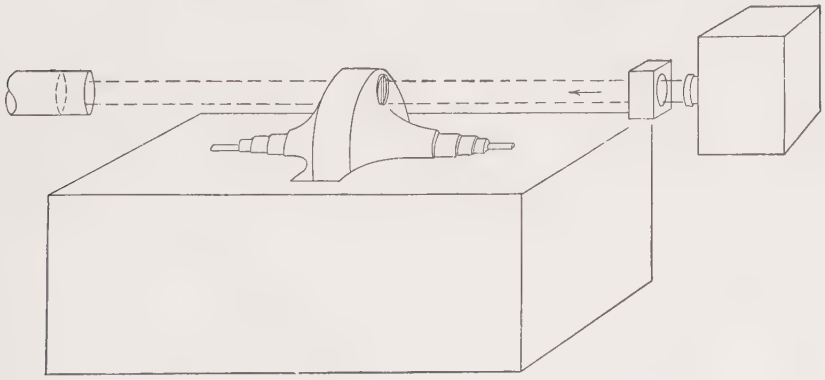


FIG. 121. Principle of the Svedberg ultracentrifuge.

methods are used to record the position of the boundary between solvent and solution at suitable intervals. Exact measurements on the photographic plate are then used for calculating the rate at which the colloid particles move. If all the particles are not of the same size, a sharp boundary cannot be obtained, even if diffusion is minimized. It is of great importance to eliminate vibrations and the convection currents

which arise normally from thermal gradients within the cell. These and other difficulties have been overcome by Svedberg.*

The specific sedimentation velocity in centimeters per second per unit centrifugal field is a characteristic of the colloid particle.

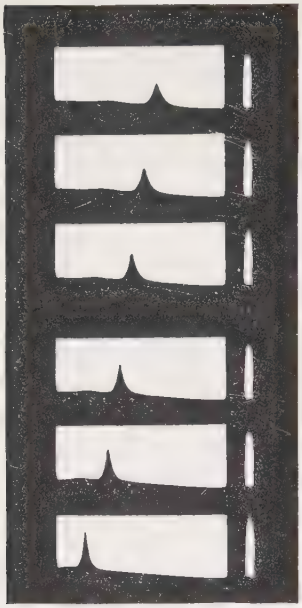


Fig. 122. Movement of colloidal thyroglobulin at ten-minute intervals while being centrifuged.

The specific sedimentation velocity of thyroglobulin may be calculated from the measurements of Lundgren and Williams shown in **Fig. 122.** This biological material was purified and mixed with a clear solution of the same acidity. The beam of light passed directly through the cell as it was rotated in the centrifuge, but, as the colloid moved outward, it left a line of demarkation where the refractive index was different so that the light was refracted out of the optical line, leaving a dark ridge. As the centrifuging progressed, this heavier material gradually moved toward the outer edge of the cell, shown by a sharp vertical shadow at the right. Pictures were taken every 10 minutes, starting at the bottom of Fig. 122 and measurements on the position of the peak showed that the boundary moved 7.2 mm in 50 minutes. There was a temperature correction η_t for viscosity amounting to 0.90. The speed of the centrifuge was 40,000 rpm, and the distance from the center of rotation was 6.4 cm. The sedimentation constant s is calculated as follows:

$$s = \frac{\frac{dx}{dt}}{\omega^2 x} \times \eta_t = \frac{\frac{0.72}{50 \times 60}}{\left(2\pi \times \frac{40{,}000}{60}\right)^2 \times 6.4} \times 0.90$$

$$= 19.2 \times 10^{-13} \text{ cm per second per unit field} = 19.2 \text{ svedbergs}$$

The particle size cannot be calculated and used without further information, because two molecules of like weight but different shape will have different sedimentation constants. Particle sizes may be obtained, however, from observations of sedimentation velocity and diffusion con-

* Svedberg and Pedersen, The Ultracentrifuge, *Chem. Rev.*, **20**, 81 (1937); "The Ultracentrifuge," Oxford University Press, Oxford, 1940.

stant made independently of one another. In dilute solutions the frictional resistance to sedimentation and diffusion is the same, so that, if a diffusion measurement is used to evaluate this resistance, it is not necessary to make any assumption regarding the shape of the particle and the particle size can be calculated directly. With the new high-speed instruments, centrifugal forces as high as 400,000 times gravity are available, and observations of the sedimentation velocity may be made in a few hours.

Some of the results obtained with Svedberg's methods are given in Table I.

TABLE I

Weights of Colloid Particles

Protein	Particle Weight	Protein	Particle Weight
Egg albumin	40,500	Phycocyan	279,000
Hemoglobin	68,100	Phycoerythrin	292,000
Serum albumin	66,900	Amandin	329,000
Lactoglobulin	37,800	Thyroglobulin	675,000
Pepsin	39,200	Hemocyanin (*Octopus*)	2,785,000
Insulin	35,100	Hemocyanin (*Helix*)	6,630,000
Serum globulin	150,000		

Simple motor-driven or air-driven centrifuges find important uses in separating colloids from solution and from mixtures of other colloids. The measurements of particle size in the more elaborate centrifuges have given us valuable information concerning the proteins in normal and pathological sera, toxins and antitoxins, viruses, polysaccharides, starches, and natural and synthetic high polymers.

Electrical Behavior. Colloid particles with their large surfaces are likely to have ions attached to them. An ion induces a charge of opposite sign in a near-by molecule and will thus be held to the surface by the ion-induced dipole attraction. The ions thus *adsorbed* exert a profound influence on the stability of the colloids, particularly the lyophobic colloids. According to the simplest view, all the particles in a given colloidal solution tend to adsorb an excess of either positive or negative ions and thus acquire a charge. The particles thus repel each other and tend to prevent combination and precipitation of the colloidal material.

The situation is more complicated, however, because this layer of ions adsorbed on the surface of the colloid particle tends to attract ions of opposite sign to it, forming two layers of oppositely charged electricity

as in a capacitor. These electric fields due to ions constitute what is known as a "double layer."

According to present views, the double layer consists of two shells of ions of opposite charge. The inner shell is narrow and compact; but the outer shell is wide and diffuse, with a high concentration of ions near the inner shell and progressively lower concentration of ions as the distance from the surface of the particle increases. The inner shell adheres tightly to the particle wherever it moves, but the outer diffuse shell of oppositely charged ions can be more easily stripped off. The total potential drop between the surface of colloid particle and the main body of the solution may be divided into two parts, the first of which is the potential between the inner shell and the colloid surface. The second part, called the *zeta* or electrokinetic *potential*, applies to the potential drop through the outer shell, extending from the outer edge of the inner shell to the body of the solution. This zeta potential for the diffuse outer shell and the arrangement of ions around a colloid particle are indicated diagrammatically in **Fig. 123** where *A* represents the surface of the par-

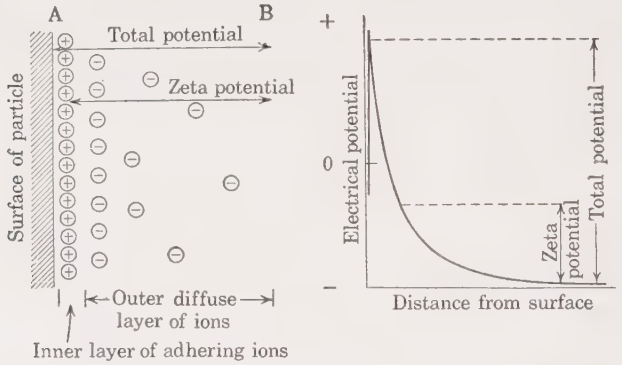


Fig. 123. Diagram defining the zeta potential in terms of a double layer of ions around a colloid particle.

ticle and *B* represents a point in the solution far removed from it. Freundlich and von Smoluchowski introduced this concept of the electrokinetic or zeta potential into colloid chemistry. It has been pointed out, particularly by Kruyt, that the stability of hydrophobic colloids runs parallel with the zeta potential.

Colloid phenomena which involve movement of a colloid particle through the solution can be described more quantitatively with the help of the zeta potential.

The zeta potential can be changed by changing the electrolytes and the colloid solution since the original inner layer of adsorbed ions and

the outer layer of oppositely charged ions which they attract are a function of the nature and concentration of the electrolytes which are present.* At high concentrations of electrolytes electrokinetic phenomena disappear because the double layer is compressed about the particle, and the increase in electrical conductivity also causes a diminution in electrokinetic action.

Electrophoresis. There are several important consequences of the existence of the potential difference in the diffuse double layer. The application of an external voltage causes the charged colloid particles to move toward one of the electrodes, and they tend to drag along with them parts of the outer diffuse shell of oppositely charged ions. Negative colloids move to the positive electrode, and positive colloids to the negative. This phenomenon is known as *electrophoresis.*

Electrophoresis was first observed by Reuss in 1807. When the terminals of an electric battery are connected to two platinum electrodes dipping into a colloidal solution of arsenious sulfide, there is a gradual migration of the colloid to the positive pole. A similar experiment with a solution of ferric hydroxide shows that this colloid moves toward the negative pole. It follows, therefore, that the particles of colloidal arsenious sulfide are negatively charged, whereas those of colloidal ferric hydroxide carry a positive charge. Most of the lyophobic colloids possess an electric charge. In water, the colloids of metals and many organic colloids acquire a negative charge, but many positive colloids are known also.

The velocity of electrophoresis can be determined by measuring the rate of movement of the boundary which separates the colloid solution from a clear solution which has been carefully run in above it. In another method a microscope is used to measure the distance traveled toward the electrode by a single colloid particle under a definite potential gradient. In measurements of electrophoresis the electrodes are usually arranged so that there is no evolution of gas which might cause mechanical stirring of the solution. For example, a cadmium electrode surrounded by cadmium ions may be used. The velocities of electrophoresis vary considerably with the conditions of the experiment, but they are of the order of 2 to 20 $\times$ 10^{-5} cm per second when the potential gradient is 1 volt per centimeter. Although the colloid particles are much larger than individual ions, the rate of movement toward an electrode in water is not so much faster as might be expected, because both drag along with them diffuse shells of oppositely charged ions. The mobility of the colloids is of the order of one-tenth that of ions. A shell of water mole-

* Abramson, "Electrokinetic Phenomena," Reinhold Publishing Corp., New York, 1934.

cules has to be pulled along also, attracted by the force which exists between a charged ion and a molecule like water which possesses a large dipole moment.

There are many practical applications of electrophoresis. The sign of the charge on colloids and bacteria is easily found. Certain colloids may be plated out electrically in a manner similar to the electroplating of metals, and, in fact, many rubber articles such as rubber gloves are manufactured in this manner.

Among the important developments in electrophoresis are the examination and separation of proteins, including normal, pathological,

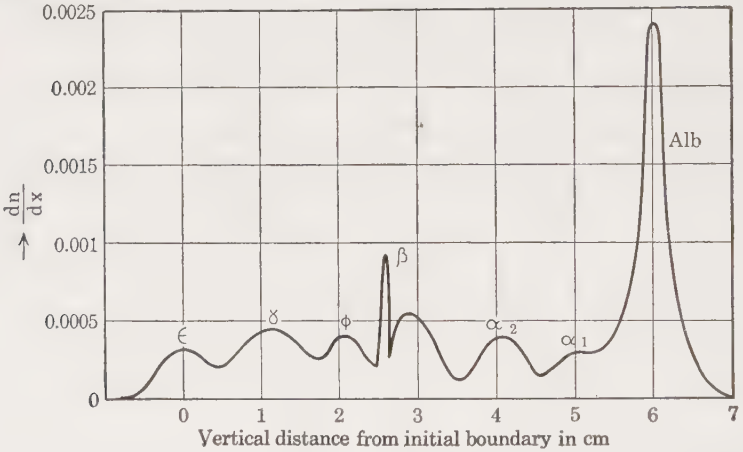


FIG. 124. Identification and separation of constituents of human blood plasma by electrophoresis. dn/dx is the rate of change of refractive index with distance.

and immune sera, and the preparation of pure biological materials. Apparatus for following the migration of these materials in an electric field has been perfected by Tiselius.* A cell is provided with flat transparent sides, and a beam of light specially focused is recorded on a photographic plate. The material frequently contains two or more materials which are so nearly alike that they cannot be separated by chemical means; yet when placed between two electrodes they move at slightly different rates. The light passes through the colloid solution and the clear solution adjoining it without deflection, but at the line of demarkation between two solutions the light is refracted to one side leaving a dark region. After a time the different colloid materials move along to different distances and give optical patterns similar to that shown in **Fig. 124** for

* Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937); *Biochem. J.*, **31**, 1464 (1937).
Tiselius, Electrophoretic Analysis and the Constitution of Native Fluids, *Harvey Lectures Ser.*, **35**, 52 (1939).

the electrophoresis of human blood plasma as measured by Professor Robert Alberty of the University of Wisconsin. In his experiment the plasma was subjected to a potential gradient of 9 volts per centimeter for 152 minutes in a buffer solution of *p*H 8.6 and 0.10 ionic strength. The vertical ordinates represent rate of change of refractive index with distance, and the peaks correspond to the sharpest boundaries between materials of different refractive index. Along the horizontal axis is plotted the distance in cm to these sharp boundaries, starting with a reference point ϵ at the extreme left which corresponds to the original position of the salt boundary. The peak at the extreme right corresponds to albumin, and the other peaks correspond to various constituents of the plasma.

The characteristic pattern may be used for identification of a mixture and for determination of purity. A uniform material having colloids of only one size and charge gives a single dark band. A colloidal protein or other material may be not only identified but also purified by electrophoresis. For example, it may be found that only one of the substances gives the desired biological effect, and this material can then be withdrawn from the remaining solution when the shadow of its boundary passes a specified exit tube.

Electroosmosis. In electrophoresis the solution is stationary, and the colloid particles move under a potential gradient. In electroosmosis the colloid material is held in position, and the solution moves when an electric potential is applied. Finally, if the colloid surfaces are held mechanically stationary and the liquid is forced through a colloid membrane or porous plate, a potential difference will be produced at the two sides of the membrane. This potential difference may be measured and is known as the *streaming potential.* All three properties are connected with the zeta potential.

Electroosmosis can be illustrated with an experiment in which a porous partition, containing a large surface area acting as colloid material, is placed in the bottom of a U tube which contains an electrode in each arm. When the tube is filled with water or other suitable liquid, and the electrodes are charged, the water rises in one arm and falls in the other as a result of electroosmosis. An equilibrium height is reached which is proportional to the applied voltage. Usually but not always in electroosmosis the water moves toward the cathode, showing that the fixed colloid material acquires a surplus of negative ions, leaving the solution positively charged. The experiments have been extended to organic liquids as well as to aqueous systems. The drying of peat and other material by the application of an electric field has been suggested; but there is a large loss of electric energy if electrolytes are present to conduct the current.

Stability of Colloids. The most important factors in stabilizing colloids are electric charge (zeta potential) and hydration or solvation. Either the existence of a zeta potential which causes the particles to repel each other or a film of adsorbed solvent which prevents the enclosed particles from touching each other is sufficient to keep the dispersed particles in the colloidal state. In the lyophobic colloids, where there is little attraction between the dispersed particles and the dispersion medium, the film is not a factor, and the stability or instability of the colloid depends only on the presence or absence of a diffuse layer of ions about the particle. The relation between the lyophylic colloids and the lyophobic colloids is well illustrated in **Fig. 125.** The lyophilic

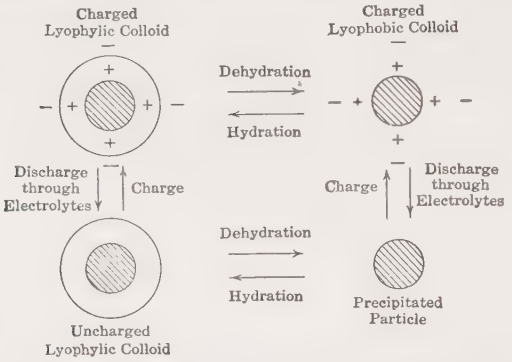


FIG. 125. Illustration of the role of electric charge and hydration in the stabilization of colloids.

colloid particles are solvated, that is, they attract around themselves an atmosphere of the dispersion medium, whereas the lyophobic colloids do not. Either the electrical double layer, or the hydrating atmosphere, or both together keep the system in the colloidal state. The particles become coagulated, and the system loses its colloidal properties only when both the electrical double layer and the hydrating atmosphere are removed. Egg albumin may be taken as an example. Its particles can be dehydrated with alcohol, and the electric charge can be neutralized by the addition of ions, but only when *both* changes are effected does coagulation occur.

The ability of dispersed particles to remain in the colloidal state is greatly affected by the concentration of ions. In the absence of ions a lyophobic colloid is not stable, and the material will settle out. The presence of a few ions stabilizes the colloid, but, if there is a large excess of electrolyte, the colloid particles will be coagulated by the ions of opposite charge.

The *isoelectric point* is the concentration of hydrogen ions and other ions at which the particle has no net charge and the zeta potential is zero. The isoelectric point is important because under the conditions prevailing the colloid has its minimum stability, viscosity, and electrical conductivity. Lyophilic colloids such as albumin and gelatine are particularly responsive to a change in pH, and in an acid solution they are charged positively on account of a chemical reaction and subsequent dissociation. In an alkaline solution they acquire a negative charge in the same way. The behavior is like that of amphoteric electrolytes which can dissociate to give either H^+ ions or OH^- ions.

Precipitation of Colloids by Electrolytes. Electrolytes, even in low concentrations, are effective in precipitating lyophobic colloids. The concentrations in milliequivalents per liter required to cause precipitation in 2 hours, as found by Freundlich, are recorded in Table II for a positive ferric hydroxide colloid (16 millimoles per liter) and for a negative arsenious sulfide colloid (8 millimoles per liter). In each case, 2 ml of the electrolyte was added to 20 ml of the colloid solution.

TABLE II

PRECIPITATION OF COLLOIDS BY ELECTROLYTES

Electrolyte	(+) Ferric Hydroxide	(−) Arsenious Sulfide	Electrolyte	(+) Ferric Hydroxide	(−) Arsenious Sulfide
	Conc. Electrolyte	Conc. Electrolyte		Conc. Electrolyte	Conc. Electrolyte
NaCl	9	51	$MgSO_4$	0.2	0.8
KCl	9	50	$AlCl_3$	...	0.1
KNO_3	12	50	$Al(NO_3)_3$	...	0.1
$Ba(NO_3)_2$	14	0.7	K_2SO_4	0.2	...
$BaCl_2$	10	0.7	$K_2Cr_2O_7$	0.2	...

It is evident that the trivalent ions are much more effective in precipitating colloids of opposite sign than are divalent ions and that the divalent ions are more effective than the univalent ions. There is no simple quantitative relation between the valence of the ion and the precipitating concentration because several other factors are involved also, such as the protective action of ions having the same sign as the colloid particles.

Table II illustrates the general principle that positive colloids are precipitated by negative ions and negative colloids are precipitated by positive ions; and in both cases the higher the valence of the ion (that is, the larger the number of charges on a single ion), the more effective is the precipitation.

The action of electrolytes on lyophylic colloids is less sharply defined than their action on lyophobic colloids. Large concentrations of alkali salts are necessary to precipitate albumins; but small amounts of the heavy metals give precipitation on account of chemical reactions.

Charged colloids as well as ions are effective in precipitating colloids of opposite charge. For example, when solutions of positive ferric oxide colloids and negative arsenious sulfide colloids are mixed, a mutual precipitation of the two colloids is produced. Sometimes the mixture of two different kinds of ink will cause a precipitation for the same reason.

Protective Colloids. When a lyophylic colloid is added to a solution of a lyophobic colloid, it often forms a coating around the lyophobic colloid, owing to attraction of the two colloids. The lyophobic colloid surrounded by the film of lyophylic colloid then behaves as a lyophylic colloid, and is thus less easily precipitated by ions. Protective coatings of this kind can be illustrated by the stabilizing effect of gelatine added to lyophobic colloids such as sulfur or freshly precipitated silver bromide. They are found in organic colloids, and they play a part in the behavior of certain cements and even in the geology of certain sedimentary rocks. In biological systems they are particularly important.

The protective action of a lyophylic colloid can be measured semiquantitatively by finding the concentration of the colloid which is necessary to just prevent the change in a solution of colloidal gold from red to blue produced by the addition of a specified amount of sodium chloride. This concentration, sometimes called the "gold number" of the protecting colloid, is sufficient to form a protective coating which will prevent the gold particles from growing into larger crystals when an electrolyte is added. The formation of the larger particles in the solutions of colloidal gold is accompanied by a change from red to blue.

Interfacial Tension. When two partially miscible liquids are placed in contact, each dissolves to a certain extent in the other, sometimes causing marked changes in the surface tensions. The interfacial energy may be defined as the work required to increase the area of the interface by 1 sq cm.

It can be measured by most of the methods already described for measuring the surface tension of pure liquids against air. The drop-weight method, in which the weight of a drop of the first liquid is deter-

mined as it falls or rises from a specially prepared tip immersed in a second liquid, is perhaps the simplest for measuring interfacial tensions. The conditions have to be carefully controlled. The addition of a third substance which concentrates in one or both liquids at the interface may exert a profound influence on the interface and on the colloidal behavior.

Gibbs' Equation. The influence of concentration of solute on the surface tension of the solution was derived in 1876 by Gibbs.* It is summarized by the equation,

$$u = -\frac{c}{RT}\frac{d\gamma}{dc} \tag{10}$$

where u is the excess concentration of solute in the surface layer per square centimeter, and $d\gamma/dc$ expresses the rate of change of surface tension with concentration. According to this equation, in a solution in which the surface tension increases with concentration (that is, $d\gamma/dc$ is positive) solute is forced out of the surface layer and into the interior of the solution by the addition of more solute; but in those solutions where the addition of more solute decreases the surface tension the added solute will tend to concentrate in the surface layer.

It may be concluded that the surface tension of a liquid can be lowered to a considerable extent by the addition of a solute because the solute will then concentrate in the surface and register a large effect; however, the surface tension can never be increased very much by the addition of a solute because, in this case, it is held chiefly by the bulk of the solution where it can exert no influence on surface phenomena. This deduction is well confirmed by experiment. Soaps and other material are known to reduce the surface tension of water by more than half, but no substance has yet been discovered which will raise the surface tension more than a few per cent.

Experimental tests of this equation are difficult because the real surface layer contains such a small amount of dissolved material, but they indicate that the equation is essentially correct. In one of the tests, froth and foam were swept out from a soap solution, and the concentration in this froth was found to be greater than that in the bulk of the solution left behind,† in another, a scoop traveling along an accurately machined track skimmed off the surface of the solution.‡

Adsorption. At the extreme surface of a solid there must be a layer of atoms and molecules which have some valence forces or other attractive forces left over that are not so fully utilized as those associated

* Gibbs, *Trans. Conn. Acad.*, **3**, 439 (1876).

† Nutting, Long, and Harkins, *J. Am. Chem. Soc.*, **62**, 1496 (1940).

‡ McBain and Wood, *Proc. Roy. Soc.* (*London*), **A 174**, 286 (1940).

with the atoms and molecules in the interior which are completely surrounded by other molecules. Accordingly, most solids attract gases or solutes to their surface, a phenomenon which is called adsorption. The extent of this adsorption depends greatly on the specific nature of the adsorbing solid and the molecules being adsorbed, and it depends also on the concentration or pressure and on the temperature. Since adsorption is a surface phenomenon, it depends on the area of the surface exposed.

Charcoal is an excellent adsorbent for the removal of condensable vapors from gases or for the removal of solutes from solution. The cellular structure of the plant or animal material from which the charcoal is made provides a very large surface area if care is taken in the production of the charcoal. Organic or inorganic precipitates can be prepared with many crevices and capillary pores in the surface, thus giving a large surface area and a large capacity for adsorption. Silica gel, described a little later, is an example of such an adsorbent.

For a given weight of adsorbent with a given surface area the amount of material adsorbed depends on the concentration of the material around the adsorbent. The higher the concentration, the greater the amount which can be adsorbed. When an adsorbing material is placed in contact with a suitable gas or solute, the amount adsorbed will gradually increase, and the concentration of the surrounding molecules will decrease until the rate of desorption becomes equal to the rate of adsorption, and, thus, an equilibrium is established. If the concentration of material is increased, the weight of adsorbed material will increase to a new equilibrium value, and, if the concentration is decreased, the adsorbent will lose adsorbed material to its surroundings until equilibrium is again established. This relation is illustrated in **Figs. 126** and **127** for the adsorption of nitrogen dioxide on silica gel (NO_2 and N_2O_4 calculated as NO_2).

Adsorption of this type may often be represented by the empirical equation of Freundlich, which applies either to gases or to solutes in solution,

$$\frac{x}{m} = kc^n \tag{11}$$

or

$$\log \frac{x}{m} = n \log c + \log k \tag{12}$$

where k and n are constants to be determined by experiment for each temperature, solute, and adsorbent. Graphs for this equation are shown in Fig. 127, and the evaluation of the constants is illustrated in example 4.

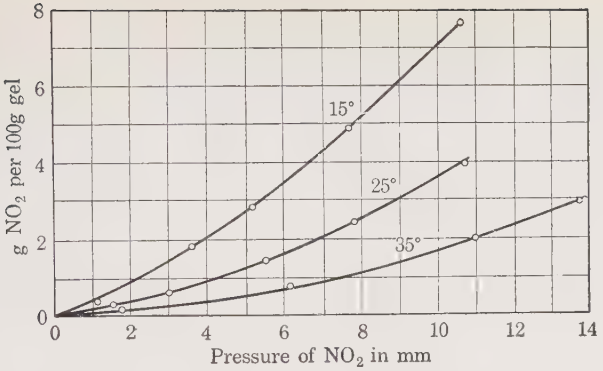


FIG. 126. Adsorption of nitrogen dioxide on silica gel.

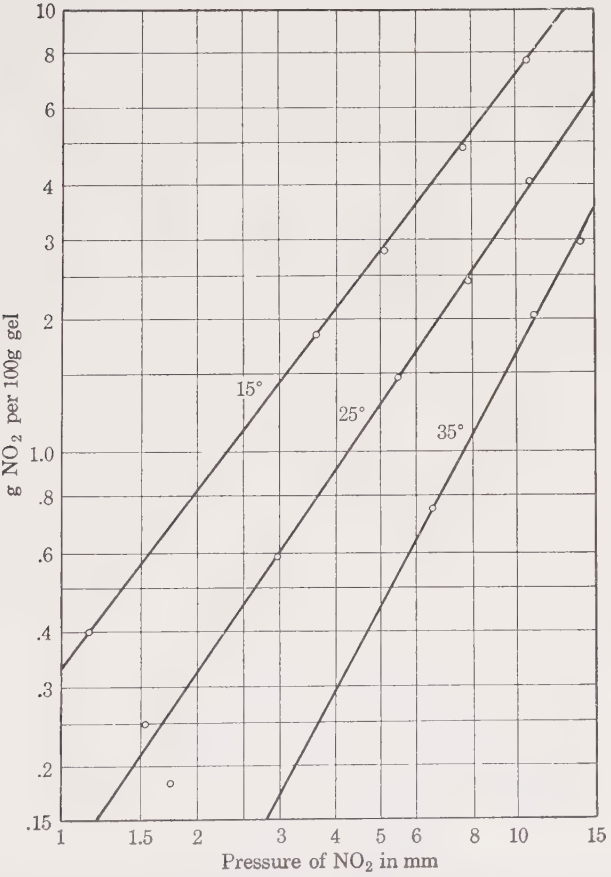


FIG. 127. Log—log graph of adsorption of nitrogen dioxide on silica gel using data of Fig. 126.

Example 4. Evaluate the constants k and n in Freundlich's equation, for nitrogen dioxide using the following data at 25°.

p (in mm pressure)	3.00	5.4	7.7	10.6	12.3
x/m (in g NO_2 per g SiO_2)	0.54	1.37	2.35	3.92	5.01

When the logarithms of these data are plotted on rectangular coordinates, the slope of the line n is found to be 1.55. The constant k is the antilogarithm of the intercept where $p = 1$ mm and $\log p = 0$. Its value is 0.095. Then

$$\frac{x}{m} = 0.095p^{1.55}$$

Techniques are available for determining the absolute surface area of certain adsorbing materials and catalysts by measuring the amount of helium or other gas adsorbed under special conditions of low temperature and pressure.*

Industrial applications of adsorption are important. Colored material and impurities are removed from sugar and from many organic products by filtering through charcoal or other adsorbents. Obnoxious gases or valuable gases may be collected by passage through charcoal or silica gel and can be recovered later in a concentrated form by raising the temperature and desorbing the gas. Gas masks containing adsorbents are used for protection against specific poisonous gases.

Some adsorbing materials exchange specific ions as, for example, the zeolites which are used in water softening. Where the reaction is

$$X\begin{matrix}\diagup \\ \diagdown\end{matrix}\begin{matrix}Na^+ \\ Na^+\end{matrix} + Ca^{++} \rightleftarrows X{=}Ca^{++} + 2Na^+$$

When water containing calcium ions is passed through a bed of zeolite containing a large surface, the calcium ions replace the sodium ions and are removed from the solution, the sodium ions taking their place. The zeolite can be reactivated, however, by throwing off the calcium ions with a concentrated solution of sodium ions.

Zeolites suitable for such purposes occur as natural minerals, or they can be made artificially. Other similar materials can be prepared which remove ions of iron. A new type of adsorbing material is now available in the form of organic resins such as "Amberlite" resins or "Dowex" which can be prepared in such a way as to remove specific ions or other solutes.

The Langmuir Theory of Adsorption. The Freundlich equation is useful as an empirical formula, but a better equation has been developed

* Brunauer, Emmett, and Teller, *J. Am. Chem. Soc.*, **60,** 309 (1938); Emmett, *Ind. Eng. Chem.*, **29,** 639 (1945).

by Langmuir.* Its derivation is based on the well-established view that a solid has a crystal lattice and that its surface is like a checkerboard with atoms arranged in orderly fashion. Each atom at the surface has free valences or unattached forces which are available for attaching one and only one molecule from the gas phase or from solution. There is a continuous flight of molecules from the external phase to the surface and in the opposite direction. The rate at which molecules are adsorbed depends on three factors: (1) the number s striking the surface per second (calculated from the kinetic theory of gases); (2) the fraction m of incident molecules which adhere; and (3) the area $(1 - g)$ which is not covered by adsorbed molecules, g being the fraction covered. The rate of desorption is gr, where r is the rate of evaporation from a completely covered surface.

At equilibrium,

$$gr = ms(1 - g) = ms - gms$$

$$g = \frac{ms}{r + ms}$$

Substituting l for the constant m/r, we have

$$g = \frac{ls}{1 + ls} \tag{13}$$

If different constants a and b are used, the weight of adsorbed material y per unit surface of adsorbing material is given by the formula,

$$y = \frac{abp}{1 + ap} \tag{14}$$

where p is the pressure of the gas. Concentrations c may be used instead of pressures, and y may be considered proportional to the weight of adsorbed material per weight of adsorbing material.

This formula fits many experimental data very well. In fact, the agreement constitutes an argument in favor of the underlying assumption of an adsorbed layer 1 molecule deep. At very high pressures it does not always apply so well, probably because under these conditions a new type of adsorption is occurring, namely, the liquefaction of the gas in capillary pores. Under these conditions the layer is, of course, many molecules deep and there is other evidence of condensation. Patrick found that, on silica gel, where the capillary type of adsorption prevails, the quantity of different gases adsorbed under similar conditions depends chiefly on the boiling point. Taylor has been able from

* Langmuir, *J. Am. Chem. Soc.*, **38**, 2267 (1916); **40**, 1361 (1918).

thermal measurements to distinguish between (1) chemical adsorption by attachment to an atom at a surface, and (2) physical adsorption. The evolution of heat in (1) may be several times that in (2).

It is significant that improved experiments tend more and more to support the Langmuir formula and its underlying hypotheses when the adsorption is not too great. Measurements of the quantity of water adsorbed on glass surfaces seemed to indicate that the layer must be several molecules deep, but repetition of the work with fresh glass surfaces that had never been etched by contact with liquids showed that the adsorbed layer is probably 1 molecule thick.* In an important series of investigations in which adsorbed material was weighed with a small spiral spring of quartz, McBain † has shown that, if the adsorbing surface is absolutely clean the Langmuir formula applies satisfactorily, whereas the Freundlich formula can be applied, if the adsorbing surface contains impurities. Additional proof of the correctness of Langmuir's formula is due to Tiselius.‡

Differential Adsorption. § The rate and extent of adsorption on a given adsorbent varies for different materials. When a solution containing several different substances is poured through a column of the adsorbent, each substance is adsorbed at a different level. For example, if a green leaf is extracted with acetone or petroleum ether and the solution is poured through a tube containing powdered sugar, followed by a little pure acetone or petroleum ether, the tube will show different bands of color corresponding to the carotenes, chlorophyll A, chlorophyll B, and other colored compounds. The column may then be cut apart in sections to separate the different materials adsorbed from the solution. Since most of the work to date has been done with colored substances which can be seen, the process is called *chromatographic adsorption.* It provides a simple effective method for the separation of biological materials which are otherwise difficult to separate.

Alumina, magnesia, powdered glass, charcoal, and other adsorbents may be used. Colorless materials can be separated also, if the lines separating the different materials can be brought out by fluorescence or by ultraviolet photography. Tiselius has described a modification of this method in which the solution is forced through an adsorbing column under conditions such that the materials are slowed down but not

* Frazer, Patrick, and Smith, *J. Phys. Chem.*, **31,** 897 (1927).

† McBain and Britton, *J. Am. Chem. Soc.*, **52,** 2198 (1930).

‡ Tiselius, *J. Phys. Chem.*, **40,** 223 (1936).

§ Cassidy, *J. Chem. Education*, **16,** 88 (1939); Strain, "Chromatographic Adsorption Analysis," Interscience Publishers, New York, 1941; Zechmeister and Cholnoky, "Principles and Practice of Chromatography," John Wiley & Sons, 1941.

entirely adsorbed. The moving column of filtrate is then examined with a beam of light, as in the measurements of electrophoresis described on page 542. Dark lines separate the solutions of the different dissolved materials, and, as they move along the tube, the solution between two of these dark lines is drawn out through a side arm. In this way one dissolved material may be separated from the others. Tiselius,* using

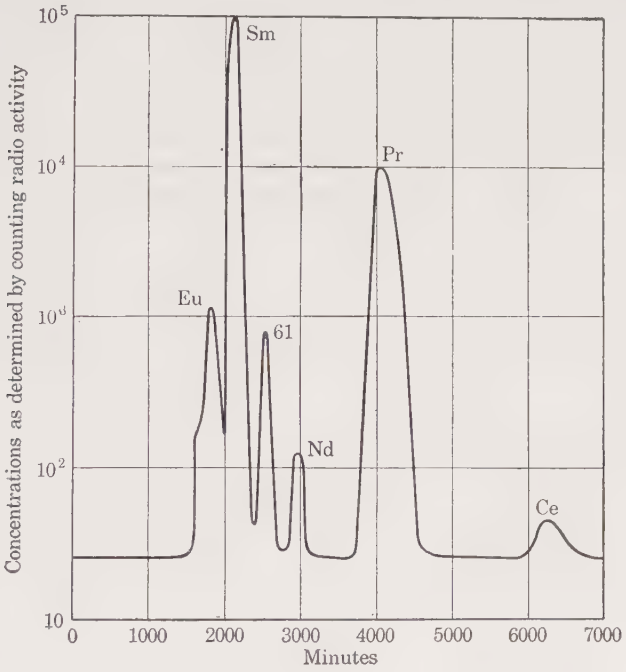


FIG. 128. Differential adsorption and elution of rare earths.

charcoal, has separated glucose from a mixture of glucose and lactose by this method.

The successful separation of the rare earth elements in a high degree of purity by fractional adsorption on organic resins is one of the striking developments of the war research.† Previous to this development the separation of the rare earths was very difficult and required hundreds of tedious recrystallizations because the different elements are so similar in their chemical and physical properties. In the new process a solution of ammonium citrate at a definite *p*H containing several of the rare earths is run through a column packed with small pieces of these or-

* Tiselius, *Arkiv. för kemi, mineralogi o geologi*, [15B] **6**, 1–8 (1941).

† Symposium on Ion Exchange Separations, *J. Am. Chem. Soc.*, **69**, 2769–2878 (1947).

ganic resins. The rare earths are adsorbed on the resin, and then they are removed by desorbing with a solution of ammonium citrate. This process of desorption is called *elution*. The equilibria and rates of adsorption and reaction with ammonium citrate are sufficiently different for the different rare earths so that a slight separation is effected while traveling a short distance down the column (corresponding to a theoretical plate as described on page 215). The separation is increased successively as the solution flows down the whole length of the column, in the same manner as gases and liquids are separated by fractionation through a long distilling column. An example of this technique * is shown in **Fig. 128.** It is interesting to note the good separation of element 61 produced by the fission of uranium 235 (page 656). Previous evidence for element 61 was not regarded as satisfactory.

Molecular Orientation at the Interface. When one drop of oleic acid or a similar oil is placed on absolutely clean, grease-free water, it spreads out quickly to give an extremely thin layer. The edges of the film are made visible by dusting talc or a similar powder over the surface, and the area then can be readily measured. The weight and density of the liquid and the area of the film being known, the thickness may be calculated easily. Moreover, the number of molecules can be calculated from the weight of the liquid and Avogadro's number. When films spread so far that they do not spread further, it may be assumed that the layer is only 1 molecule thick. Then the average cross section of a molecule can be calculated from the area, and the average length of the molecule can be calculated from the thickness of the film. A few values obtained in this way are summarized in Table III.

TABLE III

Dimensions of Molecules in Unimolecular Films

Film	Formula	Film Thickness (Length of Molecule)	Area, sq A
Palmitic acid	$C_{15}H_{31}COOH$	24 A	21
Stearic acid	$C_{17}H_{35}COOH$	25	22
Cerotic acid	$C_{25}H_{51}COOH$	31	25
Tristearin	$(C_{18}H_{35}O_2)_3C_3H_5$	25	66
Cetyl alcohol	$C_{16}H_{33}OH$	22	21
Myricyl alcohol	$C_{30}H_{61}OH$	41	27

* Ketelle and Boyd, *J. Am. Chem. Soc.*, **69**, 2808 (1947).

It is seen that the cross-sectional area of an aliphatic chain is about 22 sq A and that the compounds with three chains in the molecule have areas of 66 sq A. Increasing the length of a chain with more carbon atoms causes a corresponding increase in the film thickness. Moreover, the length and cross section of the molecules calculated in this way are in excellent agreement with the values obtained independently by X-ray analysis of crystals and in other ways. These facts support the hypothesis that the film is exactly 1 molecule thick, and closely packed, the longer axis of the molecules being nearly at right angles to the surface of the water film. These measurements were among the first to provide direct physical evidence that the organic molecules are of the shape and size expected from theoretical organic chemistry.

The explanation of this vertical alignment of molecules at the interface was offered by Harkins and by Langmuir. A molecule such as stearic acid has a polar carboxyl group at one end of a hydrocarbon residue. There is a strong dipole attraction between the carboxyl group and the water molecules but little attraction between the hydrocarbon part of the molecule and water. In simpler language, the carboxyl end of the molecule tends to dissolve in the water and the hydrocarbon portion does not. The result is that the molecules become orientated with their "heads" attached to the water and their "tails" aligned vertically. This hypothesis of vertical alignment and close packing has been checked by direct measurements with reflected X rays. This orientation at an interface is exhibited not only by the organic acids but also by the higher alcohols and any insoluble material which has a polar group on one part of the molecule. It is responsible for a variety of phenomena in colloid chemistry and biology.

The force exerted by these unimolecular films has been measured accurately with simple apparatus.* A barrier is forced against the film in a special trough, and the force required to compress the film by definite area increments has been measured with a special balance. On plotting the force in dynes against the areas per molecule, expressed in square angstroms, curves are obtained for these two-dimensional films which exhibit breaks at definite pressures.

Langmuir † has carried out interesting experiments with these unimolecular films, in which the pressure of the film causes it to deposit along the surface of the plate as the plate is passed through the film into

* Langmuir, *J. Am. Chem. Soc.*, **39**, 1869 (1917); Harkins, "Recent Advances in Surface Chemistry and Chemical Physics," Am. Assoc. Adv. Sci., Science Press, New York, 1939, page 29.

† Langmuir, "Recent Advances in Surface Chemistry and Chemical Physics," Am. Assoc. Adv. Sci., Science Press, New York, 1939, page 1; *Science*, **84**, 379 (1936).

or from the water. By dipping a clean plate of glass up and down through the surface film, it is possible to build up multiple layers which finally become thick enough to show interference patterns with light. From the wave length of the light reflected through these films it is possible to determine the total thickness, and from this value and the number of films deposited it is possible to calculate the length of the molecule in the film. This value agrees with the length calculated in other ways.

The Donnan Membrane Equilibrium.* Certain colloidal substances, such as congo red, are alkali salts of complex organic acids, and they dissociate, for example, into Na^+ and R^- ions. The anions of such *colloidal electrolytes* are so large that they cannot pass through membranes such as parchment paper. The sodium ion, however, can diffuse through, but the diffusion can proceed only to a slight extent before it is offset by the large electrostatic attraction, because of the creation of unbalanced positive and negative charges on each side of the membrane. When sodium chloride is present, however, the Na^+ and Cl^- ions can diffuse through in pairs without upsetting the electrical equilibrium. When a mixture of congo red and sodium chloride is placed on one side of a membrane and sodium chloride alone on the other side and time is allowed for the attainment of equilibrium, it is found that the concentration of the R^- ion remains the same, but the total concentration of ions is greater on the congo-red side. The quantitative relations between the concentrations of the various ions and the osmotic effects have been developed by Donnan (originally also by Willard Gibbs) and checked

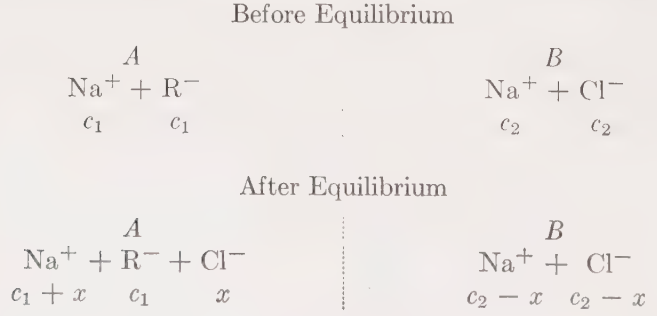


FIG. 129. Principle of Donnan membrane equilibrium.

by experiment. These relations can be described with the help of **Fig. 129** where the ions Na^+ and R^- at concentrations c_1 are placed on one side A of a membrane permeable to water and to all ions except the colloidal R^- ions.

* Donnan, *Chem. Rev.*, **1**, 73 (1924).

On the other side, B, of the membrane, sodium chloride is placed at concentration c_2.

It is assumed that both salts are practically completely dissociated. The R^- ions cannot diffuse through the membrane, and their concentration remains constant at c_1, but the other three ions are free to diffuse and at equilibrium will have definite concentrations, determined by two restrictions. According to the first restriction, the number of positive ions and negative ions must be equal in a given solution, insuring electric neutrality.

According to the second restriction, the product of the concentrations of sodium ions and chloride ions must be the same in solutions of sodium chloride which are at equilibrium.

When equilibrium is reached, x ions of Cl^- and x ions of Na^+ will have diffused into the compartment A, leaving $c_2 - x$ ions of each in compartment B.

Then, since

$$(c_{Na^+} \times c_{Cl^-})_A = (c_{Na^+} \times c_{Cl^-})_B$$

$$x(c_1 + x) = (c_2 - x)(c_2 - x)$$

and, therefore,

$$\frac{x}{c_2} = \frac{c_2}{c_1 + 2c_2}$$

The term x/c_2 gives the fraction of sodium chloride which diffuses through the membrane.

Example 5. In the membrane experiment just described, if the initial concentration of congo red in A is 10 (in arbitrary units), and that of sodium chloride in B is 20, what will be the concentration of each ion in each compartment after equilibrium is attained?

$$x = \frac{c_2^2}{c_1 + 2c_2} = \frac{400}{10 + 40} = 8$$

Then at equilibrium; in A, $c_{Na^+} = 18$, $c_{R^-} = 10$ and $c_{Cl^-} = 8$; and in B, $c_{Na^+} = 12$ and $c_{Cl^-} = 12$.

It is clear that the two restrictions previously mentioned are met: $18 = 10 + 8$ and $12 = 12$; and $18 \times 8 = 12 \times 12$.

The Donnan membrane equilibrium finds several applications especially in the field of biology. It is particularly applicable to proteins and the lyophilic colloids. It explains the observed differences in concentration and the swelling of gelatine. Since the total concentration of solutes is greater on the side of a membrane containing ionizable col-

loids, it is clear that the vapor pressure will be less, and there will be diffusion of water into the solution of greater concentration.

The interaction of slow and rapidly moving charged particles involves a Donnan effect just as if the particles and ions were separated by a membrane instead of by a difference in velocities. The Donnan effect may be suppressed by the addition of an excess of neutral electrolytes which diminish the zeta potential. In this way it is possible to obtain measurements in the sedimentation of proteins which are characteristic of the protein itself rather than of the assembly of protein-stabilizing ions.

Emulsions. An *emulsion* is a system of two immiscible liquids, one of which is dispersed throughout the other in small drops. If the drops of the dispersed liquid are large, they settle rapidly, and the liquids quickly separate into two layers. If the diameter of the drops is between 1μ and 0.001μ, the system is colloidal, and the emulsion is much more stable.

In order to prepare stable colloid emulsions, it is usually necessary to add a small amount of an *emulsifying agent*, such as a soap, which will reduce the surface tension of one of the liquids. Obviously, the introduction of a large number of small drops of another liquid within the body of a liquid increases greatly the surface area of the first liquid, and it is clear that the energy required for such a surface expansion will be less if the surface tension is decreased. In the case of benzene and water, the interfacial tension of 35 dynes per centimeter can be reduced to 2 dynes per centimeter by the addition of sodium oleate. By such procedures it is possible to obtain emulsions which have 100 parts of oil spread out as drops through only 1 part of water. Emulsifying agents include not only soaps and detergents which reduce surface tensions but also gelatine, albumin, gum arabic, and other lyophylic colloids which tend to form protective coatings around the small drops. Sometimes unsuspected impurities act as emulsifying agents in the formation of emulsions which would not otherwise be expected.

The oil-in-water emulsion is a common type of emulsion, but it is possible also to have water-in-oil emulsions. The liquid forming the drops is called the *dispersed liquid*, and the external liquid in which the drops are dispersed is called the *dispersion medium*. In a simple test to determine which is the dispersion medium, a drop of each liquid is added to a sample of the emulsion spread out on a plate. If water mixes with the emulsion, the water is the dispersion medium; if oil mixes with it, the oil is the dispersion medium. The type of emulsion formed will depend somewhat on the relative solubilities of the emulsifying agent in the two liquids. For example, pure magnesium oleate which is soluble

in benzene but not in water lowers the surface tension of the benzene and gives an emulsion of water dispersed in benzene.

Emulsions find many industrial applications. Mechanical homogenizers are used to mix two immiscible liquids intimately by producing very fine droplets of one in the other. For example, asphalt emulsified in water is used for building roads without the necessity of melting the asphalt. One of the most important processes now used in mining operations for concentrating the valuable part of ores is that of ore flotation. In this process the finely pulverized ore is treated with an oil emulsion and foam in such a way that the particles of valuable mineral are carried to the surface where they are collected.

Among the household emulsions milk and salad dressing are important examples. The cleansing action of ordinary soap depends to a large extent on the production of an oil-in-water emulsion in which the large surface of the oil droplets helps to remove the greases and dirt. Several drugs are prepared in the form of emulsions.

Emulsions are sometimes objectionable, as, for example, in oil wells which give petroleum emulsified with water. Emulsions often can be broken by freezing, by filtration, by electrostatic precipitation, and by centrifuging. The centrifuge method is used extensively for the separation of cream from milk.

Gels. A given material may be produced in either the crystalline or amorphous state, depending on the conditions of its formation. Von Weimarn has shown that the degree of supersaturation, at the time of formation, and the viscosity of the medium account for the observed phenomena qualitatively at least. For example, when barium sulfate is precipitated from very dilute solutions it is possible to obtain small crystals. When the solutions are more concentrated, the state of supersaturation after mixing is greater, and the crystals become less pronounced. When the solutions contain about 1 equivalent per liter, an immediate precipitate is formed which is apparently amorphous. With still more concentrated solutions (3 to 7 equivalents per liter of barium thiocyanate and manganese sulfate), a clear jelly is produced.

It is obvious then that we should not speak of crystalloidal and colloidal matter but rather of the crystalloidal and colloidal states. In fact, it is now recognized that it is simply a matter of overcoming experimental difficulties before it will be possible to obtain most forms of matter in the colloidal state.

A *gel* is a stiff semirigid precipitate which retains the liquid in which it was initially dissolved. Gels may be prepared in several different ways. The simplest and commonest type of gel is produced by cooling a certain type of colloid solution. For example, when a 2 per cent solution of

gelatine dissolved in warm water is cooled, it sets to a stiff transparent gel in which long filaments of material are intertwined in a structure resembling that of a pile of brushwood. Gels may be made also by direct precipitation, in which there is a direct exchange of ions such, for example, as the silicic acid gel, which is produced by mixing solutions of hydrochloric acid and sodium silicate. After the combined solution stands for a while, it sets to a stiff clear gel, the time required for setting depending on the concentrations. It is this silicic acid gel which after being dried gives silica gel with many pores and large surface areas that are effective in the adsorption of gases.

Another type of gel is produced by changing the solvent. A gel of nitrocellulose is formed, for example, when chloroform is mixed with a colloid solution of nitrocellulose in amyl acetate. Again the nitrocellulose gel can be prepared by dissolving nitrocellulose in acetone and evaporating the solvent. The threadlike nature of the cotton can sometimes be detected even after the gel has been formed, indicating that the original character of the fibers still persists and that these fibers can retain large amounts of the liquid. Double-base "powder" used extensively as a propellent in large naval guns and in rockets is a gel composed of nitrocellulose and nitroglycerol.

On standing, gels frequently undergo an appreciable shrinkage in volume with a simultaneous extrusion of liquid. This phenomenon is called *syneresis*. When placed in a dry atmosphere gels quickly dry out, and when placed in water they take up water, rapidly at first, and then more slowly. The rate depends on the difference between the weight of water which the gel holds and the maximum amount which it can hold.

The change of sol to gel is a reversible one in the case of gelatine. The gel is readily reconverted into a sol on warming the stiff gel obtained when a moderately concentrated solution of the gelatine is cooled. In albumin and certain other lyophilic colloids, however, a chemical change accompanies the heating, and irreversible coagulation occurs, as exemplified in the boiling of an egg.

The behavior of gels on freezing depends largely on the amount of unadsorbed water, and this relation is important in explaining the winter hardiness of certain types of seeds.

Lyotropic Series. Salts have a marked effect on the temperature of the gel-sol transformation, some tending to raise the temperature of gelation and others to lower it. The effect is not to be explained on the basis of ionic charge, and, in fact, univalent ions give widely different results. Hofmeister arranged the negative ions of sodium salts in the

following order, the first having the greatest influence in lowering the temperature of gelation and the last one the least influence:

$$SCN^- > I^- > Br^- > NO_3^- > ClO_3^- > Cl^- > C_2H_3O_2^- > SO_4^{--} \quad (15)$$

The same sequence of ions is maintained, not only in the gelation temperature of agar-agar and similar substances, but also in their rate of swelling, and the series finds applications in several different fields. The behavior of this series is not fully explained as yet, but it is related in some way to the diameter of the ion and the interaction between the ion and the dipoles of the water molecules.

Industrial Colloids. Foams consist of air bubbles surrounded by liquid films, and these become troublesome in certain industrial processes of evaporation. Clouds and smokes are colloid particles of liquids or solids dispersed in the gas phase. They tend to obscure vision and produce dirt in cities; sometimes they are responsible for large financial losses in chemical operations, and again they may constitute health hazards to animals and plants. A successful method of electrical precipitation, invented by Cottrell, is extensively used in smelting and other industries where a valuable or an objectionable dust or smoke passes out the chimney. A direct current at about 50,000 volts is passed from a central wire to the surrounding circular metal wall in the form of a corona discharge. The particles acquire electric charges by attaching ions in the discharge and are quickly drawn to the electrodes from which they can then be scraped mechanically.

Proteins, dyes, and soaps constitute a group of colloids of known chemical structure. They are among the smallest colloid particles, and, in fact, the difference here between true solution and colloid solution is not sharply defined. These materials frequently dissociate into ions and are called colloidal electrolytes. A surprisingly large number of common articles are gels including cellophane, rayon, soap, resins, rubber, and many new plastics.

REFERENCES

Kraemer, "Colloid Science," Interscience Publishers, New York, 1942.
Svedberg, "Colloid Chemistry," Chemical Catalog Co., New York, 1928.
Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York.
Weiser, "Colloid Chemistry," John Wiley & Sons, New York, 1939.
Mark, "Physical Chemistry of High Polymeric Substances," Interscience Publishers, New York, 1940.
Colloid Symposia, *J. Phys. Chem.*, 1930–47.
Freundlich, "Colloid and Capillary Chemistry," E. P. Dutton and Co., New York 1926.

PROBLEMS

1. In a colloidal solution of silver, it is assumed that each particle is a cube 0.04μ on an edge. (*a*) How many colloid particles can be produced from 0.1 g of silver? (*b*) What is the total area of the silver particles? (*c*) What is the area of a single cube of silver weighing 0.1 g? The density of silver is 10.5.

Ans. 1.49×10^{14} particles. (*b*) 1.43×10^4 cm^2. (*c*) 0.268 cm^2.

2. Using the following modification of Stokes's law

$$\mu = \frac{2gr^2(S - S_0)}{9\eta}$$

where μ = velocity; g = force of gravity; r = radius of particle; S = density of particle; S_0 = density of medium; η = viscosity of medium; calculate the time necessary for a quartz particle 10μ in diameter to fall 50 cm in distilled water at room temperature. $S = 2.6$; $\eta = 0.0100$ poise. *Ans.* 95.6 minutes.

3. A sample of polystyrene was dissolved in toluene, and the following flow times in an Ostwald viscometer at 25° were obtained for different concentrations:

Concentration (g/100 cc)	0	0.1	0.3	0.6	0.9
Time (seconds)	86.0	99.5	132	194	301

The expression $[(n/n_0) - 1]/c$ is plotted against c and extrapolated to zero concentration to obtain the intrinsic viscosity. If the constants in Staudinger's equation are $K = 3.7 \times 10^{-4}$ and $a = 0.62$ for this polymer, calculate the molecular weight.

Ans. 640,000.

4. Human blood plasma contains approximately 40 g of albumin ($M = 69{,}000$) and 20 g of globulin ($M = 160{,}000$) per liter. Calculate the colloid osmotic pressure at 37° C ignoring the Donnan effect. *Ans.* 14 mm of mercury.

5. One milliliter of a certain activated charcoal has a surface area of 1000 sq m. If complete surface coverage is assumed, as a limiting case, how much ammonia, at standard conditions, could be adsorbed on the surface of 45 ml of activated charcoal? The diameter of the NH_3 molecule is 3×10^{-8} cm, and it is assumed that the molecules just touch each other in a plane. *Ans.* 18.5 liters.

6. Magnesium oxide adsorbs silica from water and follows the Freundlich equation. It may be used to reduce boiler scale of silica. Plot the following data on log–log paper and calculate the constants of the Freundlich equation. Calculate the parts per million of magnesium oxide needed to reduce the residual silica to 2.9 parts per million. (1 ppm = 1 mg per 1000 g H_2O.)

MgO (ppm)	0	75	100	200
Residual SiO_2 (ppm)	26.2	9.2	6.2	1.0
SiO_2 removed (ppm)	0	17.0	20.0	25.2

Ans. 153 ppm MgO.

---

7. A solution containing 0.0015 g of Fe_2O_3 per milliliter was diluted 1 part to 10,000. Ultramicroscopic count on the dilute solution gave an average of 4.1 particles per count in a field of view of 0.04 mm diameter and 0.04 mm depth. If it is assumed that the density of the particle is 5.2, and that the particles are spheres, what is the diameter of the particles?

8. Using the formula $\mu = [2gr^2(S - S_0)]/9\eta$ (given in Problem 2) calculate the time necessary for a spherical calcium chloride particle 40μ in diameter to fall 1 cm

in carbon tetrachloride at room temperature. ($S_0 = 1.595$; $S = 2.152$; $\eta = 0.00975$ poise.)

9. The number of spherical particles in a given volume of mercury sol which had come to equilibrium in a gravitational field was 386 at one level and 193 at a level 0.10 mm higher. The temperature was 20°. The specific gravity of mercury is 13.6, and that of the sol may be assumed to be 1. What is the average diameter of the particles?

10. Colloidal egg albumin has a particle weight of 40,500. What is the osmotic pressure at 25° of a solution containing 5 g per liter?

11. The diameter of the hydrogen molecule is 2.74 A. If an adsorbent has a surface of 850 sq m per milliliter and 95 per cent of the surface is active, how much H_2 (measured at standard conditions) could be adsorbed by 100 ml of the adsorbent? It may be assumed that the adsorbed molecules just touch in a plane.

12. One hundred grams of oleic acid ($C_{17}H_{33}COOH$) is poured on the surface of a clean lake where the spreading film can be seen if the water is rippled by a gentle wind or marked with rain drops. The cross section of the molecule is about 22 A^2. What will be the maximum diameter in meters of a circular film produced in this way?

13. From the Langmuir equation show that y is a linear function of p at very low pressures, and independent of p at very high pressures and that the curves of the equation will approximate roughly in general shape the Freundlich adsorption isotherm.

---

14. A mercury sol is composed of globules having a diameter of 0.07μ. What is the surface of the particles formed from 1 g of mercury?

15. A gold sol has particles of radius 15 A. Calculate the specific diffusion constant of this sol in water at 25°. The viscosity of water is 0.00895 poise.

16. What is the osmotic pressure in millimeters at 25° of a 0.3 per cent colloidal solution of gold if the particles are cubical and 25 A on an edge?

17. Crystallized serum albumin is dissolved in 0.1 N buffers of several different pH for the experimental measurements of electrophoresis. The distance moved by the protein boundary in the electrophoretic cell during 2 hours at a potential gradient of 6.5 volts per centimeter are given in the following table. Plot

pH	3.76	4.20	4.82	5.58
Δx (cm)	0.936	0.328	0.234	0.700
	Movement toward cathode		Toward anode	

the protein ion mobility versus pH, and determine the isoelectric point by interpolation. *Ans.* pH of 4.5.

18. The adsorption of N_2 on mica is as follows:

p	2.8	6.1	17.3	23.8
x/m	12	19	28.2	30.8

(p is given in dynes per square centimeter and x/m is the cubic millimeters of gas at 20° and 760 mm adsorbed on 24.3 g of mica, having a surface of 5750 sq cm.) Determine the constants of Freundlich's equation, and calculate the value of x/m when $p = 34$. (The experimental value of $x/m = 33$.)

19. Show that Langmuir's equation may be written in the form $p/y = 1/ab + p/b$, where $y = x/m$. The constants a and b may be determined from the data of Prob-

lem 18 by plotting p/y against p. The straight line thus obtained has a slope $1/b$ and an intercept $1/ab$. What are the values of the constants, and what is the calculated value of y when $p = 34$ dynes per square centimeter?

20. A liter of 0.01 M gelatin chloride "G" Cl is placed on one side of a membrane and a liter of 0.1 M sodium chloride on the other. After equilibrium is reached, what will be the concentration of sodium ion and chloride ion on each side of the membrane? The membrane is permeable to sodium ions and chloride ions but not to gelatin ions.

21. When a given volume of olive oil was dropped through a standard tip into a 0.001 M NaOH solution, 44 drops were formed, and the interfacial tension between olive oil and 0.001 M NaOH was computed to be 7.3 dynes per centimeter. When the same volume of olive oil was dropped through the same standard tip into an aqueous solution 0.001 M in NaOH and 0.15 M in NaCl, 300 drops were formed. Calculate the interfacial tension between olive oil and an aqueous solution 0.001 M in NaOH and 0.15 M in NaCl.

22. The concentration c of colloid particles in a sedimentation equilibrium can be calculated from a standard differential equation,

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} - v\frac{dc}{dx} = 0$$

where x is linear distance and D and v are constants. This equation finds many applications in the flow of matter and heat. Its general solution is $c = ae^{vx/D} + b$. Show that it can be used to derive equation 3 on page 531.

23. Derive equation 8 on page 536, for a state of equilibrium by setting the force of gravity acting downwards exactly equal to the force of diffusion acting upwards. Thus,

$$f_{\text{gravity}} = v(S - S_0)gn\,dx \quad \text{and} \quad f_{\text{diffusion}} = \frac{-\partial p}{\partial x}dx \quad \text{where} \quad p = \frac{n}{N}RT$$

24. In a centrifuge experiment with egg albumin in a buffered aqueous solution at a pH of 6, the boundary moved 6.3 cm in 105 minutes, as determined by direct measurement of the change in position of the photometer curves with time. The speed of the centrifuge was 57,000 rpm. The distance from the center of rotation was 6.43 cm. Show that the specific sedimentation constant for this material is 3.5×10^{-13} cm per second per unit field, after multiplying by 0.81 to correct for density and viscosity.

CHAPTER XIX

QUANTUM THEORY

The quantum theory, first proposed by Planck in 1900, has had a profound influence on the development of science. The theory has led to advances in practical work no less important than those in theoretical work, and its findings have been so revolutionary as to lead to a new viewpoint in philosophy. There are two main themes in quantum theory—first, that radiation is discontinuous, and, second, that there are restrictions imposed in the transfer of energy to molecules and electrons. The quantitative description of these restrictions has been aided by the application of mathematical formulas, sometimes called wave equations. This extension of quantum theory is known as *quantum mechanics*.

Emission and Absorption. When light strikes a substance, a portion of the incident radiation is transmitted, a portion is reflected, and a portion is absorbed. These three possibilities are illustrated by the passage of visible light through glass, the reflection from silvered glass, and the absorption by smoked glass.

It has been established by Kirchhoff that the ability of a given substance to emit radiation when heated is proportional to its ability to absorb radiation. Denoting the emission and absorption by E and A respectively, we have

$$E = sA \tag{1}$$

where s is constant.

The constant s is the emissivity of a *black body* or perfect radiator which absorbs all the radiation and reflects none. Thus, when absorption is complete, $A = 1$, and, according to equation 1,

$$s = E$$

A hollow sphere containing a single small hole acts as a perfect radiator with complete absorption and maximum emission of light. Practically all the radiation passing into the small opening is absorbed by multiple reflections at the surface. Likewise, when the sphere is heated, the radiation emitted has the maximum intensity that it can have at a given temperature. An electrically heated furnace with a small opening or even a heated blackened strip of platinum serves as a convenient but imperfect substitute for a perfect radiator.

The value of the emissivity constant s is the same for all solids at a given temperature, but the emission E decreases when the absorption becomes less than 100 per cent, as shown by equation 1.

It can be shown that the law of Kirchhoff is a necessary consequence of the application of the second law of thermodynamics to the thermal equilibrium within an enclosure, the walls of which are impervious to heat.

Kirchhoff's law may be illustrated with a spot of colored glass melted onto a colorless glass tube. The spot appears dark on account of the absorption of light, but when the tube is heated the spot appears brighter than the rest of the tube because, according to equation 1, the emission E is directly proportional to the absorption A. When the tube is placed inside a heated furnace with a small opening, however, the spot disappears because the temperature has become uniform throughout and light is reflected back and forth so as to make the absorption of light complete within the enclosure.

Laws of Radiation. According to the Stefan-Boltzmann law, the total radiation E emitted by a perfect radiator is proportional to the fourth power of the absolute temperature.

Thus,

$$E = \sigma T^4 \tag{2}$$

where σ is constant having the value 5.69×10^{-5} erg cm^{-2} sec^{-1} deg^{-4}. This law, discovered experimentally by Stefan and derived theoretically later by Boltzmann, has been abundantly verified. A simple test consists in measuring on a cold receiver the quantity of heat radiated per second from a small opening of known area in a heated furnace.

Example 1. An electrical furnace heated to 727° has a small hole 2 sq cm in area which is pointed at a cold receiver. How many calories of heat hit the wall in an hour?

$$E = 5.69 \times 10^{-5} \times 2 \times 3600 \times \frac{(1000)^4}{4.184 \times 10^7} = 9790 \text{ cal}$$

The receiver itself radiates heat so that the net heat absorbed is less than this.

The average radiation from the summer sun on the surface of the earth has been found to be approximately 1.2 cal per minute per square centimeter in temperate zones. It has been estimated that the temperature of the surface of the sun is about 6200° K, the center of course being very much hotter.

Total radiation includes radiation of all wave lengths, visible, infrared, and ultraviolet. The intensity of the radiation from a perfect radiator

varies greatly with the wave length as shown in **Fig. 130.** Measurements of this type may be made by spreading out with a suitable prism the total radiation from a perfect radiator. A thermopile is then moved along in different parts of the spectrum, and with suitable corrections

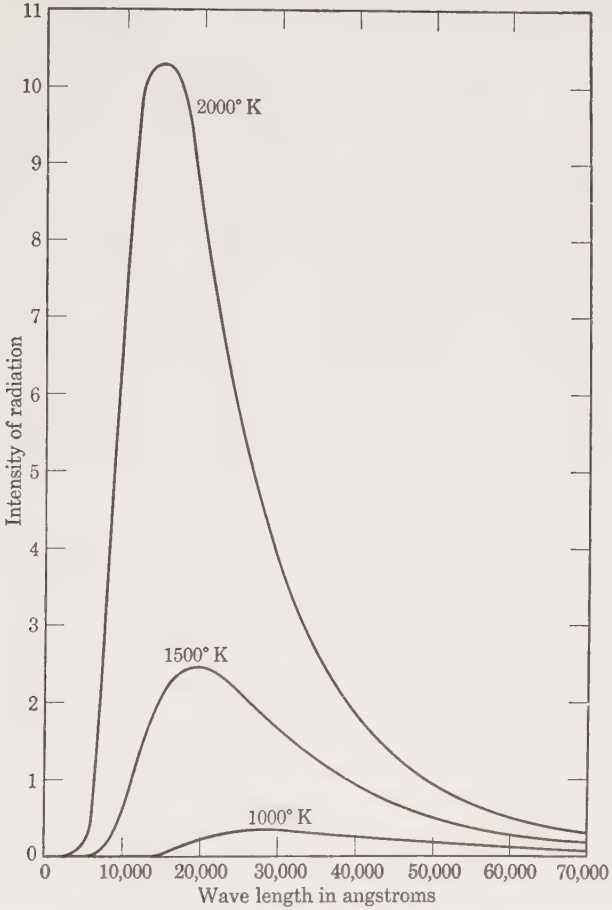


FIG. 130. Emission of radiation from a black solid at different temperatures. The area under a curve, divided by 10,000, between specified wave lengths gives the energy in calories per second radiated from 1 cm^2 of a perfect radiator.

the deflections of the galvanometer connected to the thermopile are proportional to the intensity of radiation.

When an ordinary solid is heated, similar curves are obtained except that they fall below the curves shown in Fig. 130 for a perfect radiator. The emissivity varies with the wave length and with the nature of the solid and its surface, but it is never greater than that for a perfect radiator.

In Fig. 130 it is to be noted that, as the temperature of the perfect radiator is increased, the area under a curve corresponding to total radiation, increases as given by the Stefan–Boltzmann law. Moreover, $\lambda_{max.}$ shifts to the shorter wave lengths. Wien showed that

$$T\lambda_{max.} = A \tag{3}$$

and

$$E_{max.} = BT^5 \tag{4}$$

where $\lambda_{max.}$ is the wave length at which the maximum occurs, $E_{max.}$ is the energy radiated at $\lambda_{max.}$, and A and B are constants.

The energy E_λ is the energy in ergs cm^{-2} sec^{-1} of a small portion of the spectrum lying between λ and $\lambda + d\lambda$. Wien developed another formula which holds for short wave lengths but not for the longer wave lengths, according to which,

$$E_\lambda = \frac{C_1}{\lambda^5} e^{-C_2/\lambda T} \tag{5}$$

and Rayleigh developed a formula which holds only for the long wave lengths, according to which,

$$E_\lambda = \frac{C_3}{\lambda^5} (\lambda T) \tag{6}$$

where C_1, C_2, and C_3 are constants.

It is to be remembered that all these formulas apply only to heated bodies emitting continuous radiation.

Origin of Quantum Theory. Realizing the limitations of these formulas, Planck derived a better equation which expressed the experimental facts with remarkable exactness over the whole range of the spectrum. In deriving this equation Planck was led to the bold conclusion that radiation is emitted and absorbed discontinuously in integral multiples of a fundamental unit which he called a quantum ϵ, and that the energy of a quantum is proportional to the frequency of the light. These suggestions led to the *quantum theory*.

The development of the quantum theory is one of the important milestones in science. As in many other important advances, the exact experimental facts came first, then an empirical mathematical equation to express the facts, and, finally, a working hypothesis to explain the terms in the equation. Then, on the basis of this hypothesis, predictions were made and new experiments planned which led to rapid progress in many different fields of science. General confirmation of the hypothesis soon gave it the rank of a theory.

Planck's formula * is

$$E_\lambda = \frac{2\pi c^2 h}{\lambda^5 (e^{ch/k\lambda T} - 1)} \tag{7}$$

where E_λ is the rate of emission of radiation of wave length λ, c is the velocity of light, k is the gas constant per molecule (R/N) called the Boltzmann constant, and h is a constant now known as Planck's constant. This proportionality constant h has turned out to be a very important universal constant.

Formula 7 can be integrated to give the Stefan–Boltzmann law; it approaches the Rayleigh law, 6, for large values of λ, and it approaches Wiens distribution law, equation 5, as λ approaches zero. Moreover, it is in agreement with the Wien equation 3. Planck's radiation formula then is in remarkable agreement with the various facts of radiation, and it gives experimental values with excellent precision. In spite of these successes, the formula would probably have failed to obtain general acceptance on account of the radically new assumption concerning quanta, except for the fact that almost at once it became extremely useful in new and unrelated fields. It has revolutionized the study of spectroscopy. Critical potentials, photoelectric effects, and specific heats have all been interpreted quantitatively with the help of the quantum theory. The study of photochemistry and chemical kinetics and the calculation of equilibrium constants (page 286) have been stimulated by applications of quantum mechanics.

According to the classical theories, the energy imparted to a molecule is distributed equally among the various degrees of freedom or types of motion which the molecule, and its parts can undergo, such, for example, as rotation of the molecule, vibration of the atoms, and displacement of the electrons. This hypothesis of the equipartition of energy is now known to be inadequate. The molar heat capacity of monatomic gases at constant volume is $\frac{3}{2}R$ (page 115), and there are three possible directions and three degrees of freedom in the translational energy. Each degree of freedom then has associated with it $\frac{1}{3} \times \frac{3}{2}R = 1$ cal per degree. For each extra atom in the molecule there are more degrees of freedom and a greater heat capacity. Actually, however, the polyatomic gases have heat capacities which are much less than those calculated on the basis of the number of degrees of freedom. Also, there is nothing in the classical theory to lead one to expect the large temperature coefficient of heat capacity which is actually found. Furthermore, diatomic hydrogen gas at temperatures below 70° K has a molar heat capacity

* This formula is discussed fully in Taylor and Glasstone, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1942, pages 189–196.

of 3 cal and behaves exactly as a monatomic gas. Again, on the classical theory, crystals of solid elements should have a heat capacity of 5.9 cal per degree (page 120), but a few crystals like carbon and, in fact, all crystals at sufficiently low temperatures have a heat capacity much smaller than 5.9. Apparently some of the degrees of freedom are "frozen up" at the lower temperatures. The restricting of the degrees of freedom found an explanation in the quantum theory of restricted energy units, and formulas involving the quantum $h\nu$ were applied, with considerable success, to specific heats at low temperatures.

There seems, then, to be adequate experimental justification in many fields for the quantum theory, according to which radiation is composed of units called quanta, and the energy of each quantum ϵ is given by the fundamental equation of the quantum theory,

$$\epsilon = h\nu \tag{8}$$

where h has the value 6.624×10^{-27} erg-second and ν is the frequency of the radiation in reciprocal seconds. In many applications of the theory, quantum numbers appear as integers in the various formulas, as indicated later.

Spectroscopy. The quantum theory has had its greatest success in the interpretation of spectra, and the pioneer work is due to Bohr * who in 1913 proposed the fundamental hypothesis that electrons exist in definite energy levels, E_1, E_2, etc., without emitting or absorbing radiation, but that, when an electron changes from one level to another, monochromatic radiation is emitted or absorbed in accordance with the following equation:

$$E_2 - E_1 = \epsilon = h\nu \tag{9}$$

Bohr assumed that the electrons revolve around the nucleus in elliptical orbits and that the centrifugal force is equal to the force of electrostatic attraction. In accordance with the new ideas he assumed further that the motion of the electron was *quantized* and that instead of an infinite number of possible orbits there is only a restricted number with properties represented by functions of the quantum number n, where n is an integer 1, 2, 3, 4, $\cdots$. By a simple application of mechanics and electrodynamics, given in the appendix on page 689, he showed that the energy E_n in a particular orbit n is

$$E_n = \frac{-m(Ze)^2e^2 4\pi^2}{2n^2h^2} \tag{10}$$

where m is the mass of the electron, Z is the atomic number (page 621).

* Bohr, *Phil. Mag.*, **26**, 1, 476, 857 (1913).

e is the charge on the electron, h is Planck's constant, and n is an integer. Then, according to equation 9, the quantum of light emitted on changing from one orbit to another is given by the formula:

$$\epsilon = h\nu = E_{n_2} - E_{n_1} = \frac{2\pi^2 me^4 Z^2}{h^2}\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right) \tag{11}$$

Several of these quantities can be grouped together giving a constant known as the Rydberg constant $\boldsymbol{R}$, defined as follows:

$$\boldsymbol{R} = \frac{2\pi^2 me^4}{h^3 c} \tag{12}$$

in which c is the velocity of light, 2.9979×10^{10} cm sec^{-1}

Then, substituting into equation 11, for hydrogen with an atomic number Z of 1, gives

$$\tilde{\nu} = \boldsymbol{R}_{\text{H}}\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right) \tag{13}$$

where $\boldsymbol{R}_{\text{H}}$ has the value 109,677.58 cm^{-1} and $\tilde{\nu}$ refers to wave numbers.*

Now the visible lines in the spectrum of hydrogen had been measured accurately, and Balmer in 1885 pointed out that they could be represented by an empirical formula equivalent to the following,

$$\tilde{\nu} = A\left(\frac{1}{2^2} - \frac{1}{{n_2}^2}\right) \tag{14}$$

where n_2 is a whole number greater than 2 and A is a constant. It is obvious that equation 13 is the same as equation 14 and that it constitutes an excellent check on the theoretical calculations. In fact, the numerical value of $\boldsymbol{R}$, expressed in eight significant figures, was obtained from exact spectral measurements rather than from equation 12, because some of the constants in equation 12 are known only to one part in a thousand.

It will be noticed in equation 14 that n_2 cannot be less than 2, for then $\tilde{\nu}$ would be a meaningless negative number, and it cannot be 2, for then $\tilde{\nu}$ becomes zero. As n_2 becomes larger than 2, the corresponding value of $\tilde{\nu}$ becomes larger, but, when n_2 is already large, further increases cause $\tilde{\nu}$ to increase only very slightly, and, as n_2 approaches infinity, $\tilde{\nu}$ approaches $\frac{1}{4}\boldsymbol{R}_{\text{H}}$.

* $\tilde{\nu}$ = wave number $= \dfrac{1}{\lambda_{\text{cm}}}$ and $\lambda_{\text{cm}} = 10^{-8} \times$ wave length in A

A few of the lines of the Balmer series as calculated by equation 13 setting $n_1 = 2$ are given in Table I.

TABLE I

BALMER LINES IN THE HYDROGEN SPECTRUM

n_2	$\tilde{\nu}_{\text{calc. (vacuo)}}$	λ, $A_{\text{calc.}}$[1] (vacuo)	λ, $A_{\text{obs.}}$[1] (air)
3	15,233.02	6,564.75	6,562.8
4	20,564.57	4,862.73	4,861.4
5	23,032.33	4,341.72	4,340.5
6	24,372.83	4,102.90	4,101.8
10	x	y	.....

[1] Wave lengths are measured in air. Wave numbers $\tilde{\nu}$ are the reciprocals of the wave lengths measured in vacuo.

$$\tilde{\nu} = \frac{1}{\lambda_{\text{vacuo}}} = \frac{n_{\text{air}}}{\lambda_{\text{air}}}$$

where n is the refractive index of air. Correction terms for converting λ_{air} to λ_{vacuo} are given at different wave lengths in the International Critical Tables, McGraw-Hill Book Co., New York, 1930, Vol. VII, page 5.

The success of the Balmer formula led to further exploration, and Lyman found another series in the ultraviolet spectrum of hydrogen which is just as satisfactorily represented by formula 13, provided n_1 is given the value 1. Then n_2 has values 2, 3, 4, etc. The lines calculated from this formula are known as the Lyman series. The Paschen series occurs in the infrared, and these lines are accurately reproduced by formula 13 when $n_1 = 3$ and n_2 has values greater than 3. These series are represented diagrammatically in **Fig. 131.** Light is emitted when the electron returns from a level of high energy (large quantum number) indicated by a horizontal line to a level of lower energy.

The connection between these energy levels and the actual lines in the spectrum may be seen by comparing Fig. 131 with the spectral lines in **Fig. 132,** which are adapted from an ultraviolet spectrogram of a star by R. H. Curtiss. The same sequence of lines is observed, converging to a limit. A much larger number of lines (35) has been observed in certain stars than in laboratory experiments, because the gas pressures are low, and there is more room for the large "orbits."

The continuous emission beyond the convergence limit of the lines shown in Fig. 132 is always present, and it is particularly significant. In the region where sharp lines are obtained definite quantum restric-

tions are involved, but, when the electron is driven out to an indefinitely great distance, the electron can take with it unquantized kinetic energy which can vary continuously in magnitude and, thus, give a continuous

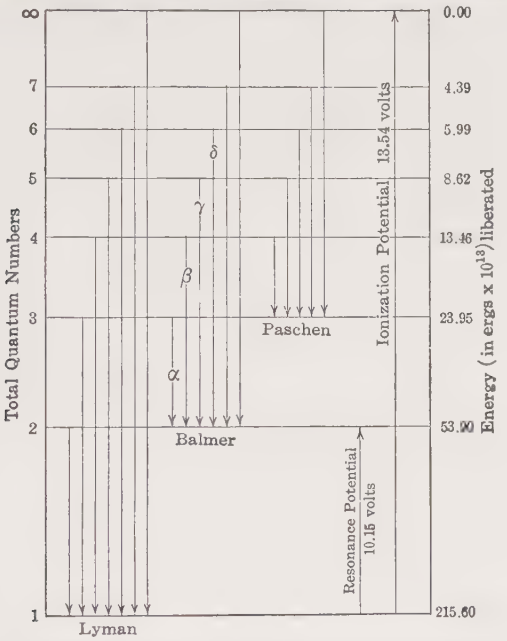


FIG. 131 Energy levels of electron in the hydrogen atom, indicated by horizontal lines.

range of frequencies. The convergence limit in the spectral series corresponds then to complete separation of the electron, that is, to ionization.

In this discussion the emission of light has been emphasized, but the absorption mechanism is the same except that the electrons are driven out to levels of higher energy by the absorption of quanta of energy, whereas in emission they fall back to levels of lower energy.

FIG. 132. Spectral lines converging to a limit beyond which there is continuous emission.

Similar formulas have been developed for helium and the alkali metals and other elements involving a single valence electron. Each element has a slightly different value of the Rydberg constant R. For helium it is 109,722.26. For the elements heavier than hydrogen and helium it is necessary to apply correcting terms, which become smaller as the quantum numbers n_2 become larger.

Bohr's formula was so successful in calculating the lines of the hydrogen spectrum with exactness that the model on which it was based was generally accepted. The elliptical orbits seemed perfectly natural by analogy with the orbits of the planets, but, of course, it does not follow that, because a mechanism gives results which agree with experimental facts, the mechanism is proved. Still other mechanisms may give the same results. In this particular case the quantum numbers are important, but they do not necessarily come from elliptical orbits. In fact, a more complicated mathematical model based on wave mechanics has now been devised which works just as well in predicting the positions of the lines and, in addition, gives the intensities of the lines and applies also to the elements heavier than hydrogen. The elliptical orbits then are not to be taken too literally.

Quantum Numbers. The spectrum of atomic hydrogen can be interpreted nicely by the simple Bohr formula making use of two numbers. Other spectra are much more complicated, and more quantum numbers are needed in calculating the spectral lines. It is found that many spectral lines have fine structure. With sufficient dispersion they are seen to give doublets, triplets, and so on. Furthermore, some of the lines are affected by a strong electrostatic field giving the *Stark effect* and by a magnetic field giving the *Zeeman effect*. In the more complex spectra some of the lines can be grouped together in overlapping series, depending on their behavior and general appearance. Thus, one series of lines is characterized by having particularly sharp lines and another by having diffuse lines. The diffuseness is due to the fact that more lines are possible because of a greater variety of energy levels, and the many lines cannot be separated except by means of a spectroscope of high resolution. Several characteristic types of spectra have come to be recognized by spectroscopists, such as the principal (p), sharp (s), diffuse (d), fundamental (f).

All these variations can be handled by using four quantum numbers. These numbers and their symbols which describe the state of an electron in an atom are as follows:

n = principal quantum number (or total quantum number)

When n =	1	2	3	4	5,
the corresponding symbols are	K	L	M	N	O.*

* These letters refer to the shells of the outer electrons as described on page 666, K referring to the first electron shell outside the nucleus, L to the second, M to the third, etc.

l = orbital quantum number

l can have any integer value, except that it must be one or more units less than the principal quantum number, that is, it can never be greater than $(n - 1)$.

When $l =$ 0 1 2 3,

the corresponding symbols are s p d f.

m_l = magnetic quantum number

m_l depends on l and may have any integral value between $+l$ and $-l$, including zero. Therefore, $2l + 1$ values of m_l are possible.

m_s = electron quantum spin number

Two values of m_s are possible, corresponding to two possible orientations of the spin vector s.* The quantum numbers can vary only by integers, and m_s can have only the values $+\frac{1}{2}$ and $-\frac{1}{2}$.

Definite physical concepts, such as the spinning of the electron, were originally attributed to these different quantum numbers, but it is neither necessary nor profitable to attach definite mechanical or electrical significance to them. They may be considered merely as arbitrary numbers which serve to describe physical and chemical facts when they are substituted into mathematical formulas.

Only those combinations of numbers are allowed which are in agreement with the restrictions just given. For example, if $n = 3$, l can be only 2, 1, or 0; and m_l can be ± 2, ± 1, or 0; and m_s can be only $+\frac{1}{2}$ or $-\frac{1}{2}$.

All the various combinations of the four quantum numbers, permitted by the restrictions just given, are recorded in Table II.

The total number of permissible combinations of the four quantum numbers is given in the last column of Table II. The recognition of these four quantum numbers has been a great aid in understanding many physical and chemical phenomena, particularly through the application of the restriction to be described in the following section.

The further application of these quantum numbers to describe complicated spectra is beyond the scope of this book. It may be stated, however, that the capital letters S, P, D, and F are used to designate electronic energy levels of atoms and that superscripts and subscripts such as ${}^2D_{3/2}$ are used to describe sub-levels.

* The spin quantum number s, used as a subscript, is not to be confused with the orbital quantum number s.

TABLE II

POSSIBLE CONDITIONS OF ELECTRONIC QUANTUM NUMBERS

Principal n	Group	Orbital l	Subgroup	Magnetic m_l	Spin m_s	Total Number of Different Combinations
1	(K)	0	(s)	0	$+\frac{1}{2}$ $-\frac{1}{2}$	2
2	(L)	0	(s)	0	$+\frac{1}{2}$ $-\frac{1}{2}$	2 } 8
2	(L)	1	(p)	+1 0 −1	$+\frac{1}{2}$ $-\frac{1}{2}$	6 }
3	(M)	0	(s)	0	$+\frac{1}{2}$ $-\frac{1}{2}$	2 } 18
3	(M)	1	(p)	+1 0 −1	$+\frac{1}{2}$ $-\frac{1}{2}$	6 }
3	(M)	2	(d)	+2 +1 0 −1 −2	$+\frac{1}{2}$ $-\frac{1}{2}$	10 }
4	(N)	0	(s)	0	$+\frac{1}{2}$ $-\frac{1}{2}$	2 } 32
4	(N)	1	(p)	+1 0 −1	$+\frac{1}{2}$ $-\frac{1}{2}$	6 }
4	(N)	2	(d)	+2 +1 0 −1 −2	$+\frac{1}{2}$ $-\frac{1}{2}$	10 }
4	(N)	3	(f)	+3 +2 +1 0 −1 −2 −3	$+\frac{1}{2}$ $-\frac{1}{2}$	14 }

Pauli's Exclusion Principle. According to Pauli, *two electrons in a single atom can never have all four quantum numbers the same.* This principle is a great help in explaining the spectral lines and the number of elements in the different groups of the periodic table. Referring to the last column in Table II, it may be seen that two different combinations of quantum numbers are possible for an s electron, six for a p electron, 10 for a d electron, and so on. Now, by the Pauli principle, there can be only one kind of atom for each given combination of electronic quantum numbers. The different atoms have different combinations of quantum states. The sequence 2, 8, 18, 32, given in the last column of Table II, is related to the sequence in the number of elements found in the successive groups of the periodic table, as shown on page 665.

Critical Potentials. When free electrons are passed through a gas at a low pressure, they must have certain velocities in order to be stopped, just as light must have certain frequencies in order to be absorbed by a given material. The energies of the electrons must correspond to definite energy transitions in the molecule, or there can be no interaction. This is a fundamental postulate of the quantum theory.

The apparatus shown in **Fig. 133** is a simple one which permits the direct experimental measurement of critical potentials. A filament is

heated to emit electrons, and an adjustable potential E_1 of several volts is applied between it and the grid G_1, the latter being charged positively. When the tube is thoroughly evacuated, the electrons coming from the filament are driven through spaces in the grid and across the tube to the plate P, whence they pass through the galvanometer to the ground. An opposing potential E_3 between the plate P and the grid G_2 is increased until the electrons are barely able to reach the plate. A trace of gas, mercury vapor, for example, is next admitted, and the slow-moving electrons suffer many elastic collisions with the molecules without loss of energy and they still reach the plate and are registered by the galvanometer. As the potential E_1 is increased gradually, the current through the galvanometer increases. Eventually, however, the current decreases suddenly because the electrons have acquired sufficient kinetic energy to cause a definite displacement of electrons from one energy level to a higher level, in the molecules of which the gas is composed. In these inelastic collisions the energy of the moving electron is all transferred to the molecules, and the electrons then do not retain sufficient velocity to reach the plate. As the potential is increased still further, the electrons acquire more energy, some of which is retained after collision. The subsequent collisions of these electrons with other molecules again become elastic, and the electrons reach the plate and register an increased current through the galvanometer.

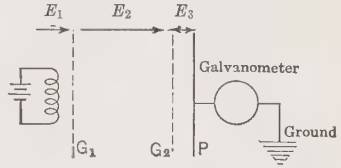


FIG. 133. Apparatus for measuring critical potentials.

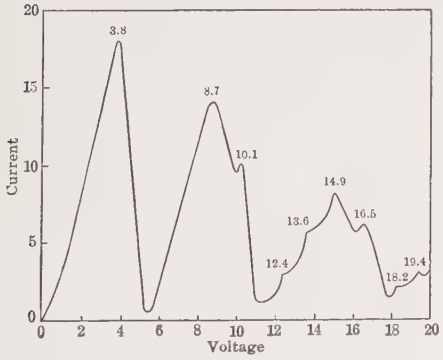


FIG. 134. Critical potentials in mercury vapor.

This process is continued as the potential is gradually increased until the electrons acquire kinetic energy sufficient to produce another displacement of the electron in the atom. Then the collisions become inelastic and the current drops abruptly as before. Several peaks corresponding to definite energy changes are observed. A curve of this type, in which electron current is plotted against the voltage, is shown in **Fig. 134,** where Einsporn's data *

* Einsporn, *Z. Physik,* **5,** 208 (1921).

on mercury vapor are given. The critical potentials are taken as the voltages at which the current first starts to decrease, but it is necessary to apply a correction to all the values shown in Fig. 134 because the electrons leave the filament with a definite kinetic energy, in this case amounting to 1.1 volts. The first critical potential then is 4.9 rather than 3.8.

The second grid G_2 and reversible potentials $\boldsymbol{E}_2$ and $\boldsymbol{E}_3$ are designed to distinguish between the two kinds of critical potentials, namely, ionization potentials and resonance potentials.

An *ionization potential* is the voltage which gives to a free electron just sufficient energy to ionize the atom or molecule, that is, to drive an electron completely out, leaving a positive ion but without imparting any kinetic energy to the electron. *Resonance potentials* are potentials sufficiently great to cause the emission of light when the free electrons are stopped by collision. They involve the displacement of valence electrons to higher energy levels and their return to lower energy levels with the emission of light in accordance with equation 9.

An obvious and simple relation among the electric energy, the kinetic energy, and the radiation energy is involved in these quantum changes, as given by the following equation,

$$\boldsymbol{E}'e = \tfrac{1}{2}mv^2 = h\nu \tag{15}$$

where e is the charge on the electron in electrostatic units (4.80×10^{-10}), m its mass, and v its velocity, and $\boldsymbol{E}'$ is the potential drop in electrostatic volts through which the electron falls. All the quantities must be expressed in the same cgs units. Since by definition one ordinary or absolute volt is equal to 300 electrostatic volts $\boldsymbol{E}/300 = \boldsymbol{E}'$, and

$$\frac{\boldsymbol{E}}{300}e = h\nu \tag{16}$$

Referring to page 571,

$$\frac{\boldsymbol{E}e}{300} = h\nu = hc\tilde{\nu} = hc\boldsymbol{R}\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right) \tag{17}$$

or

$$E = \frac{300\boldsymbol{R}hc}{e}\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right) \tag{18}$$

where n_1 and n_2 are the quantum numbers 1, 2, 3, 4, 5, etc.

This equation is used in Table III to show the numerical relation between spectral lines and critical potentials in the Lyman series of *atomic* hydrogen, where $n_1 = 1$. The constant $300\boldsymbol{R}hc/e$ has the value of 13.539.

TABLE III

SPECTRAL LINES AND CRITICAL POTENTIALS IN THE LYMAN SERIES

Quantum Number n_2	Wave Length, $A_{obs.}$	Wave Number, cm^{-1}	Volts, $E_{calc.}$	Volts, $E_{obs.}$
2	1215	82,258	10.154	10.15
3	1026	97,491	12.034	12.05
4	973	102,823	12.692	12.70
5	950	105,291	z	.....
6	938	106,631	13.161	13.17
7	931	107,440	13.262	13.27
∞	912	109,678	13.539	13.54

The agreement between the calculated and observed voltages is excellent, again strengthening the underlying quantum theory on which the calculations are based. In many cases it is possible to show the actual emission of light of the expected frequency by bombarding with electrons of the proper voltage, new spectral lines being brought in as the voltage is increased.

Electron velocities and even spectral quantities are often expressed in terms of volts, calculated with the help of equation 18. The term volt when applied to energy quantities really means electron volt per electron. The relation among electron volts, wave numbers, frequencies, angstrom units, and kilogram calories per mole is given graphically on page 599.

A beam of electrons has many of the properties of a beam of light of extremely short wave lengths. Use has been made of this fact in determining the structure of molecules (page 86) and in taking photomicrographs of objects too small to be rendered visible with a microscope and ordinary light (page 530).

The Photoelectric Effect. Light quanta can be emitted by bombardment with electrons as just shown, and it is to be expected that electrons can be emitted by bombardment with quanta of light. In 1887, Hertz discovered that, when a spark gap is exposed to ultraviolet radiation, the voltage necessary for the passage of a spark is appreciably lowered. This effect is due to the emission of electrons and the consequent ionization of the air between the terminals of the spark gap. A sheet of zinc acquires a positive charge when illuminated with ultraviolet light, owing to the emission of electrons. The ejection of electrons from a metal surface by means of light is known as the *photoelectric effect.*

This interesting effect has been utilized in the photoelectric cell, which is an extremely sensitive instrument for the detection and measurement of radiation. A diagram of such a cell is shown in **Fig. 135.**

A receiver K is coated with a thin film of potassium or other metal in a highly evacuated tube. A wire W placed in the tube is connected with the receiver through a 100-volt battery B and a sensitive galvanometer or electrometer G. The high vacuum of the tube serves as a complete insulator between W and K, but, when the receiver is exposed to light from the source S, electrons are ejected from the receiver and attracted to the positively charged wire, thus completing the circuit. The current registered by the galvanometer is directly proportional to the number of electrons released per second, and this, in turn, is proportional to the number of photons striking the receiver, that is, to the intensity of the light.

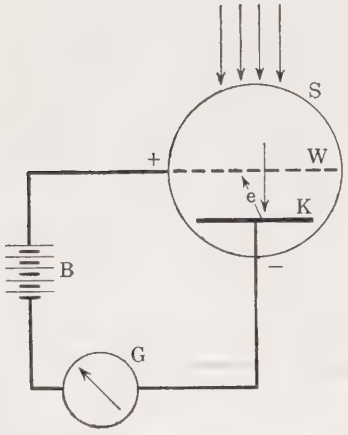


FIG. 135. Principle of the photoelectric cell.

Although the electron current or the number of electrons per second depends on the intensity of light, that is, the number of photons (quanta) striking the surface per second, the velocity or energy of the electrons driven out depends on the frequency of the light, according to the relation,

$$\tfrac{1}{2}mv^2 = h\nu - h\nu_0 = E'e \tag{19}$$

where m is the mass of the electron and v its velocity. The kinetic energy $\frac{1}{2}mv^2$ of the escaping electron is equal to $h\nu$, the energy of the incident radiation, minus $h\nu_0$, the energy required to bring the electron out to the surface of the metal. Planck's constant h has the value 6.624×10^{-27} erg-second; ν is the frequency of the incident light, and ν_0 is a constant sometimes called the photoelectric threshold.

The voltage E' in electrostatic units is the potential difference necessary to retard the velocity of the electron to zero and prevent its escape. When multiplied by the charge on the electron (in electrostatic units), the energy is just equal to the kinetic energy of the electron expelled by the absorption of the light.

When the maximum voltage E' required to prevent the production of an electron current is plotted against the frequency ν of the incident light, a straight line is obtained having a slope equal to h/e. This

relation has been accurately checked with many different metals. The experimental determination of the slope offers one means of evaluating Planck's constant h (in terms of e).

The current in a photoelectric cell can be amplified readily, with the aid of ordinary electron tubes, to operate a relay, and the photoelectric cell is finding many important applications in automatic controls, safety devices, and laboratory appliances, as well as in television and motion pictures.

New photoelectric cells of considerably greater sensitivity known as photomultiplier tubes are now available in which the electrons released by the light impinge under high voltage on a second photosensitive surface and there release additional electrons which in turn are multiplied on a third photosensitive surface. In this way just a few quanta can liberate many electrons and so give a large current to be measured.

The Compton Effect. The photoelectric effect involves the complete absorption of a quantum, but it is possible also for a quantum to impart only a portion of its energy to an electron. This phenomenon in which the energy of the photon is reduced and the energy of the electron is increased is known as the Compton effect. The photon of light collides with an electron and leaves with a lower frequency, and the electron acquires a greater velocity. Compton * bombarded carbon and other light elements with short X rays and found, with the help of a crystal lattice and spectrometer, that part of the scattered radiation had a longer wave length than the incident radiation.

This fundamental experiment, together with the realization that any physical measurement involves interaction with the measuring instruments, led Heisenberg † through mathematical considerations to the *principle of uncertainty*. According to this principle, it will never be possible to know with exactness *both* the position and the momentum of an electron or other small particle. It is not a matter of physical imperfections in the measuring apparatus but a fundamental limit of nature, according to which the error in measuring position multiplied by the error in measuring momentum is approximately of the order of Planck's constant h. The position of an electron or atom may be known with exactness, but then its velocity is unknown; and in the same way the momentum can be known only at the sacrifice of information regarding the position.

The principle is of no importance in ordinary work, because the particles involved are so large that the uncertainty is utterly negligible.

* Compton, *Phys. Rev.*, **21**, 483 (1923).

† Heisenberg, *Z. Physik*, **43**, 172 (1927).

It does have an important bearing on philosophy,* however, for heretofore it had been supposed that no *theoretical* limit was imposed on the precision of scientific measurements.

The Raman Effect. A photon of radiation may undergo elastic collision with a molecule, in which case the scattered light has the same frequency as the incident light. It may be absorbed completely in producing heat or chemical reaction; or it may contribute part of its energy to displacements of the atoms within the molecule. These atomic displacements are quantized, that is, only certain displacements are possible, corresponding to definite energy increments. Each of these quantized atomic displacements corresponds to a part of the infrared spectrum.

The *Raman effect* involves the collision of a photon with a molecule, under conditions such that there is an interchange of some of the energy of the photon. Part of the energy of the photon goes to displacing the atoms in the molecule, after which the molecule emits radiation and sinks to a lower energy level but not necessarily to the energy level which it possessed in the initial state. After such a collision the scattered radiation has a slightly different frequency from that of the incident radiation, and there is a change in the energy of atomic oscillation within the molecule. Such a collision of a photon with a molecule may then be represented by the equation

$$h\nu_{\text{incident}} - h\nu_{\text{scattered}} = \text{change in molecular energy} = h\nu_{\text{Raman}} \quad (20)$$

The difference in wave number between the incident and the scattered light permits a direct calculation of the Raman shifts. These shifts are of the order of 100 to 4000 cm^{-1}, and many of them are equal to the wave numbers at which infrared-absorption bands occur. Usually, the frequency of the scattered light is less than that of the incident light, indicating that the quantum of radiation has given up a definite small part of its energy to produce interatomic motion within the molecule. It is possible, however, for a quantum of incident radiation to absorb a small quantum of energy from a molecule and leave with greater energy. In this case $\nu_{\text{scattered}}$ is greater than ν_{incident} by an amount equal to the energy taken, divided by h.

Although the Raman lines may correspond to infrared lines, sometimes they correspond to transitions which are not directly allowed according to the restrictions of the quantum theory, that is, to frequencies which do not occur in the ordinary absorption spectrum. Valuable information concerning the nature of the spectrum can thus be obtained by combining data from both the Raman and the absorption spectra.

* Bridgman, "The Logic of Modern Physics," Macmillan Co., New York, 1927

Although this effect had been predicted by the quantum theory, it remained for Raman * in 1928 to demonstrate that the scattered light does actually contain radiation of different frequency. The difficulty lay merely in giving long enough exposure to detect the feeble Raman lines which tend to be obliterated by light of the exciting frequency. The material is placed in front of a spectrograph slit and illuminated for a long exposure with a mercury-vapor lamp (using light filters), as shown in **Fig. 136.**

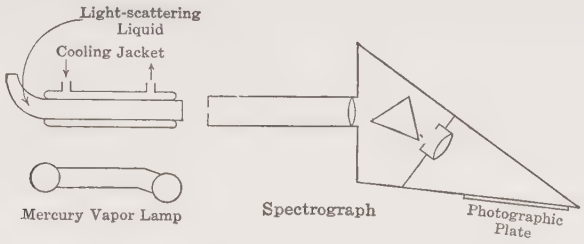


FIG. 136. Apparatus for obtaining Raman spectra.

In **Fig. 137** is shown a Raman spectrum of carbon tetrachloride obtained by Professor Paul Bender of the University of Wisconsin. The uppermost spectrum at *A* gives the standard spectrum of the mercury arc. At *B* a short exposure brings out three Raman lines clearly visible in the original spectrum plate. In a longer exposure at *C* there are four Raman lines on the long-wave-length side and three weaker Raman lines on the short-wave-length side. The former are known as Stokes lines; the latter, which involve less probable transfers of energy from excited states, are known as anti-Stokes lines. The mercury lines other than 4358 A have been filtered out except for two persistent lines showing at the right in the long exposure. At *D* is shown a photoelectric record of the Raman spectrum.† The prominent mercury line at 4358 A is so intense that the amplifier had to be made less sensitive to give a good record, as shown in the lower peak.

Raman spectra have been measured for a great many organic and inorganic compounds and complete reviews are available.‡ They are

* Raman, *Indian J. Phys.*, **2**, 387 (1928).

† Chien and Bender, *J. Chem. Phys.*, **15**, 376 (1947).

‡ Hibben, Raman Spectra in Inorganic Chemistry, *Chem. Rev.*, **13**, 345–478 (1933); Raman Spectra in Organic Chemistry, *Chem. Rev.*, **18**, 1–232 (1936); "The Raman Effect and Its Chemical Effects," Reinhold Publishing Corp., New York, 1939; Glockler, The Raman Effect, *Rev. Mod. Phys.*, **15**, 112–171 (1943). Fenske, Braun, Wiegand, Quiggle, McCormick, and Rank, Raman Spectra of Hydrocarbons, *Anal. Chem.*, **19**, 700–766 (1947).

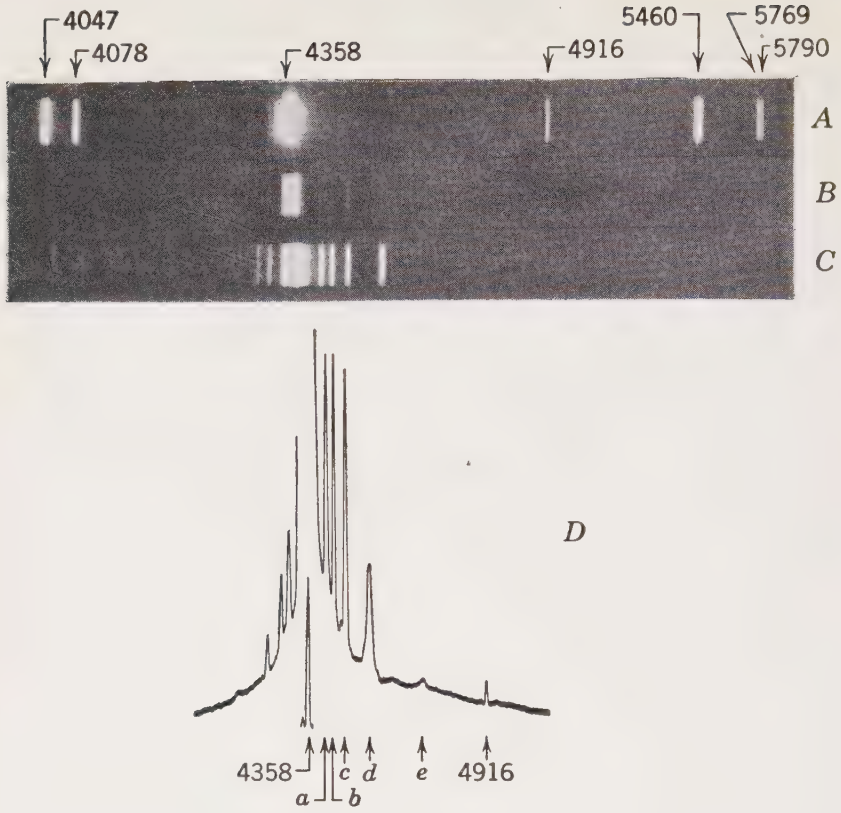


FIG. 137. Raman spectrum of carbon tetrachloride.

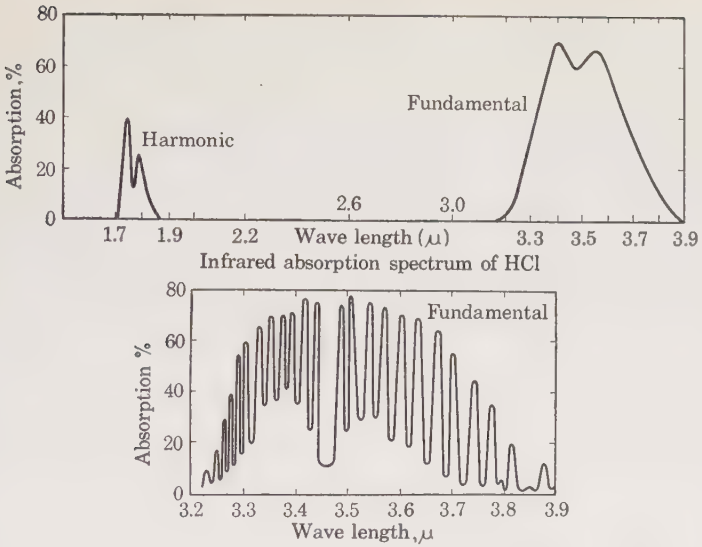
A. Mercury arc. Lines are given in angstroms.
B. Raman spectrum of CCl_4 with filter that transmits 4358 A.
C. Same as *B* with longer exposure (3 minutes)
D. Photoelectric recording of Raman spectrum of CCl_4.

$a = 4399$; $b = 4418$; $c = 4446$; $d = 4507$ and 4513; $e = 4670$ A.

helpful in interpreting molecular structure and they are useful in analytical problems.

Band Spectroscopy. So many important subjects, including heats of dissociation, specific heats, entropies, atomic vibrations, internuclear distances, intermediate compounds, and isotopes, can now be studied with the aid of band spectra that a further discussion seems justified, although a quantitative treatment is beyond the scope of this book.

A diatomic molecule of two spheres held together can be rotated by the absorption of small amounts of energy, corresponding to radiation



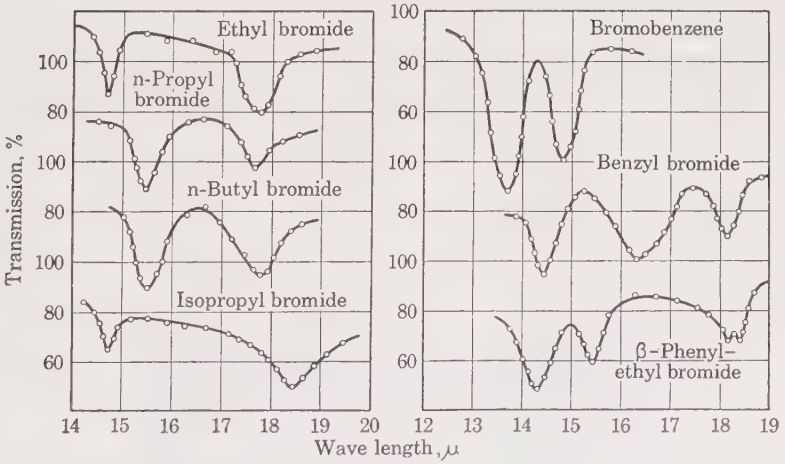


FIG. 138. Examples of infrared spectra.

in the far infrared. This rotation is quantized, and only definite amounts of energy can be added corresponding to 1, 2, 3, 4, etc., quanta of small energy.

The atoms within the molecule can vibrate, and this motion requires larger amounts of energy giving absorption in the near infrared as shown in **Fig. 138.** A diatomic molecule can rotate at the same time that two

* For the spectrum of ethyl bromide the ordinates at the right are used.

atoms are oscillating with respect to each other, and, if the molecule has an electric moment, it can be shown that the molecule will absorb frequencies of $\nu_v \pm \nu_r$, where ν_v is the frequency of vibration and ν_r is the frequency of rotation. When $\nu_r = 0$, the absorption is slight. A series of absorption lines is obtained by adding terms with quantum numbers of rotation 1, 2, 3, 4, etc., and a second series of lines is obtained by subtracting them. These two branches have maxima as indicated in the top figure of Fig. 138. The distance between these maxima permits a calculation of the distance between the atomic nuclei in the molecule.

The bands recur at definite intervals (1.75 and 3.7μ in HCl) which are governed by the integer multiples so common in quantum phenomena, except that small correcting terms are usually necessary. Under high dispersion the fine structure of the bands due to quantized rotation superimposed on vibration is apparent as shown in the center of Fig. 138.

Even in polyatomic molecules a given infrared band can sometimes be attributed to the vibration of a definite atom pair. In the lowest spectrum of Fig. 138, for example, the C–Br atom pair in several different organic bromides absorbs some of the radiation between 14 and 18μ.

These rotation–vibration spectra are often superimposed, with some distortion, on spectra caused by electron displacements, giving band spectra in the visible and ultraviolet. The lines of the band due to changes in the energy of rotation come closer and closer together, forming the head of a band.

In **Fig. 139** is shown a band spectrum obtained in the absorption of indium chloride vapor by Froslie and Winans * of the University of

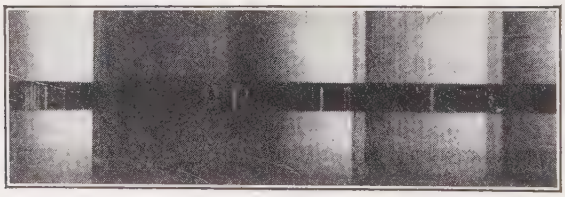


Fig. 139. Absorption spectrum of indium chloride vapor showing bands.

Wisconsin, using a 21-ft grating spectrograph. The original spectrogram shows a system of nearly equally spaced bands with alternate bands showing rotational structure and the others showing no rotational structure.

* Froslie and Winans, *Phys. Rev.*, **72**, 481 (1947).

The analysis of band spectra offers a powerful means for identifying materials, either in emission spectra or absorption spectra.

Sometimes a spectrum has a number of discrete lines adjacent to a region of continuous absorption with a definite line of demarkation between the two. From the wave length of this edge of the continuous spectrum it is possible to calculate the energy of dissociation of the molecule. Absorption spectra are discontinuous when the molecules are excited because the absorption is governed by quantum restrictions. However, when a molecule is dissociated, giving normal atoms, excited atoms, or ions, the fragments are given a certain amount of kinetic energy which is not quantized. There are no limitations on the amount of energy which can then be utilized, and radiation of all wave lengths in the region is absorbed.

FIG. 140. Absorption spectrum showing converging discrete lines due to displacement of electrons in the molecules and continuous absorption involving the dissociation of the molecule.

Accordingly, when the energy becomes great enough (the wave lengths are short enough) to cause dissociation, the absorption becomes continuous. These phenomena are indicated in **Fig. 140** where typical discrete lines corresponding to excitation are sketched at the right, heading into a band of continuous absorption at the left, corresponding to dissociation. The numbers refer to quantum numbers in the discontinuous spectrum. Just as the long-wave-length limit of continuous absorption in Fig. 132 permitted calculation of the energy of ionization of atoms, so also the long-wave-length limit of continuous absorption in band spectra permits a calculation of the energy of dissociation of the molecule. These calculations may be illustrated in the case of chlorine, which dissociates into one normal atom and one excited atom. The continuous absorption, beginning at the convergence of the discontinuous lines, occurs at 4785 A, which is equivalent to 59,400 cal per mole. The extra energy of excitation of the atom corresponds to 2500 cal as determined spectroscopically. The difference, 56,900 cal, is the energy required to disrupt the molecule, whereas direct thermal measurements give 57,000.

Energy of Dissociation. Dissociation energies can be obtained also from potential-energy curves * similar to the curve shown in **Fig. 141** for hydrobromic acid. In most chemical substances the atomic nuclei repel each other at very close distances and attract each other at large distances, but the attraction becomes less as the distance becomes very great, and it is obvious that there must be a minimum somewhere in the

* Franck, *Z. Physik*, **31**, 411 (1925).

potential-energy curve. This minimum corresponds to the most stable condition of the molecule, and, although the atoms oscillate back and forth in the molecule, they tend to keep this average distance corresponding to the minimum point.

The exact shapes of the curves ordinarily are not known, but sometimes they can be determined from the data of band spectroscopy. They

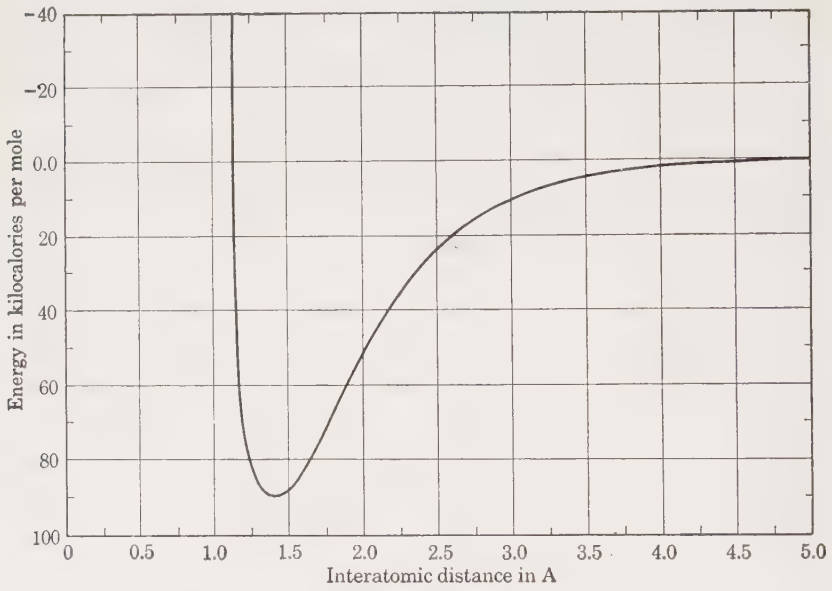


FIG. 141. Energy of HBr molecule as a function of interatomic distance.

can be calculated with the empirical formula developed by Morse *

$$E = D'(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}) \tag{21}$$

where r_0 is the distance separating the atoms in the normal molecule as determined from X-ray or electron diffraction measurements, and D' is the energy of dissociation, as determined from spectroscopy or calorimetric measurements, plus the small *zero-point energy*. The zero-point energy is the half quantum of vibrational energy which the atom pair still possesses at absolute zero. The total energy of a linear harmonic oscillator is $(n + \frac{1}{2})h\nu$ where n is an integer (vibrational quantum number) and, since energy can be lost only as whole quanta, $\frac{1}{2}h\nu_0$ remains, even at absolute zero where $n = 0$. The constant a depends on the normal vibration frequency of the atoms as determined from infrared-

* A discussion of this formula and others for calculating energies of diatomic molecules is given by Hirschfelder and Hulburt, *J. Chem. Phys.*, **9**, 61 (1941).

absorption measurements or Raman spectra and on the atomic masses. When these quantities are known, the energy E of the atom pair can be plotted against the distance r which separates the atoms. A Morse curve is shown for the hydrobromic acid molecule in Fig. 141 in which $r_0 = 1.41$ A, $a = 1.82$ and $D' = 90.0$ kcal.

Quantum Mechanics. The quantum theory is largely a theory of restrictions, and these restrictions have been determined empirically from laboratory measurements. Considerable attention was paid, therefore, to finding a theoretical foundation for these restrictions; Heisenberg and Born devised a theory based on matrix calculus and probabilities; De Broglie and Schrödinger developed a theory based on differential equations applied to waves; and Dirac embraced both in general terms with a new system of mathematics. Heisenberg's treatment and Schrödinger's treatment are both aspects of the same underlying principle, and from both the restrictions of the quantum theory come out automatically as mathematical necessities.

The Schrödinger wave equation for a simple particle is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad (22)$$

where m = mass of particle, $V_{x,y,z}$ is its potential energy in a field of force, and E is its total energy, a constant. The quantity ψ is called the "wave function" because in many problems it exhibits a wavelike series of maxima and minima. Where $|\psi|^2$ is large, there is a large concentration of electrons; in general, $|\psi|^2$ determines the probability of an electron being in a specified region. When sufficient information is available, ψ can be determined by solving the differential equation 22. The wave function is usually continuous, single-valued, and finite; and zero at infinite distance. Solutions which meet these requirements are possible only when E is given certain characteristic values, and the corresponding solutions of ψ are called *characteristic solutions.*

These characteristic values give the stationary states of the Bohr atomic model, and, thus, the quantized energy levels come automatically from the Schrödinger wave equation.

Quantum mechanics is much superior to the older theories because, in addition to accomplishing all that they accomplished, it solves more complicated problems and in many cases gives better agreement with experiment. It has led to many new advances, only two of which are mentioned here.

On the basis of the wave equations, electrons as well as radiation may be considered as waves. Davisson and Germer showed in 1925

that streams of electrons do have properties attributed to waves and like X rays may be refracted by a single crystal and that the wave lengths depend on the voltage in agreement with theoretical calculations. There is evidence that beams of protons and of neutrons (page 660) have certain properties of waves and give diffraction patterns with a crystal lattice. It appears then that matter, electricity, and radiation are composed of discrete particles—atoms, electrons, and quanta. However, in all three cases a group of these particles taken together may exhibit the properties of waves.

One of the most striking achievements of quantum mechanics was the prediction that hydrogen should exist in two different forms, which are now called ortho- and para-hydrogen. It was predicted that the space wave functions of diatomic molecules with like nuclei can be either symmetric or antisymmetric, depending on the spins of the nuclei. Evidence for the two forms was found in band spectra, where alternate lines were missing or very weak, and in the abnormal specific heats of hydrogen at low temperatures.

Bonhoeffer and Harteck * succeeded in separating these two forms and in demonstrating the difference in specific heat and other properties. At room temperature ordinary hydrogen is a mixture of three parts of ortho-hydrogen (antisymmetric type) and one part of para-hydrogen (symmetric type); at the temperature of liquid air the equilibrium is approximately 1 to 1, and at the temperature of liquid hydrogen the ortho-hydrogen is not stable and goes almost entirely into the para- or symmetric form, when catalyzed with charcoal.

REFERENCES

Glasstone, "Text-Book of Physical Chemistry," D. Van Nostrand Co., New York, 1947, pages 31–97 and 563–580.

Herzberg, "Atomic Spectra and Atomic Structure," Prentice-Hall, New York, 1937.

Taylor and Glasstone, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1942, Chapter II.

Pauling and Wilson, "Introduction to Quantum Mechanics," McGraw-Hill Book Co., New York, 1935.

Pittsburgh Staff, "An Outline of Atomic Physics," Second Edition, John Wiley & Sons, New York, 1937.

Richtmyer and Kennard, "Introduction to Modern Physics," McGraw-Hill Book Co. New York, 1947.

PROBLEMS

1. A hollow box, with an opening of 1 sq cm area, is heated electrically.
   (*a*) What is the total energy emitted per second at 800° K?
   (*b*) How much energy is emitted per second if the temperature is 1600° K?

* Bonhoeffer and Harteck, *Z. physik. Chem.*, **43**, 113 (1929).

(*c*) How long would it take the radiant energy emitted at this temperature, 1600° K, to melt 1000 g of ice?

Ans. (*a*) 2.34×10^7 ergs centimeter^{-2} second^{-1};
(*b*) 3.74×10^8 ergs centimeter^{-2} second^{-1};
(*c*) 8950 second.

2. Add 1.1 volt to values given in Fig. 134, and compare some of them with multiples of 4.9. (Other peaks involve multiples or combinations of a potential at 6.7.)

Ans. 4.9; 9.8; 14.7.

3. Calculate the velocity of an electron which has been accelerated by a potential of 1.00 volt. The mass of an electron at rest is 9×10^{-28} g.

Ans. 5.96×10^7 centimeters second^{-1}.

4. The mass m of a body moving with velocities approaching that of light is related to the mass m_o when the body is at rest by the following equation based on the theory of relativity

$$m = \frac{m_o}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

where v is the velocity of the body and c is the velocity of light. The rate of change in kinetic energy E of a moving body is the rate of change in momentum multiplied by the velocity. Prove that $dE = c^2 dm$. It was shown by Einstein in 1906 that, in general, $E = mc^2$.

5. Calculate (*a*) the wave length of the first two lines of the Lyman series; (*b*) the wave length of the first line of the Paschen series.

Ans. (*a*) 1216; 1024 A. (*b*) 19,000 A.

6. What is the wave length of light emitted when electrons are stopped after falling through a potential of (*a*) 400 volts? (*b*) 3 volts?

Ans. (*a*) 30.8 A. (*b*) 4112 A.

7. An experiment on the emission of photoelectrons from a sodium surface by light of different wave lengths gave the following values for the potentials at which the photoelectric current was reduced to zero:

A	E (volts)
5461	−2.045
4339	−1.488
4047	−1.295
3651	−0.914
3125	−0.382
2535	+0.52

Plot voltage against frequency, and determine Planck's constant from the slope of the line.

---

8. If 10,000 cal are lost per minute by radiation from the door of an electrically heated furnace at 900°, how many more watts of electricity must be applied to offset the losses due to radiation if the furnace is heated to 1100°?

9. Absorption by the fundamental vibration of the hydrochloric acid molecule occurs at 3.64μ.

(*a*) What is the frequency of light of this wave length?
(*b*) What is the energy of one quantum of light of this wave length?
(*c*) What is the value of this wave length in terms of electron volts?

10. Calculate the value of the Rydberg constant R and the constant $300Rhc/e$ for hydrogen, and compare it with the experimentally determined value.

11. There is a Brackett series in the hydrogen spectrum where $n_1 = 4$. Calculate the wave lengths, in angstroms, of the first two lines of this series.

12. Electrons are accelerated by 100,000 volts in an X-ray tube. To what wave length in angstroms does this energy correspond, when converted into radiation?

13. (*a*) Prepare a rough calibration chart for the spectrograph used in obtaining Fig. 137. Plot wave lengths of the mercury arc given in spectrum *A* against a linear scale starting at 4047 A.

(*b*) Estimate the wave lengths of the anti-Stokes lines at the left in Fig. 137*C* by interpolation on this calibration curve.

(*c*) Calculate these anti-Stokes lines exactly from the data for the Stokes lines given in Fig. 137*D*.

---

14. An electric heater of 10 sq cm is heated to 800°. How many calories of radiant heat is emitted per minute, if a perfect radiator is assumed?

15. Calculate the frequency and the wave length of the sixth line in the Balmer series of hydrogen for which the electron falls from the eighth quantum level to the second.

16. Calculate the frequency and the wave length in angstroms for the line in the Paschen series of the hydrogen spectrum which is due to a transition from the sixth quantum level to the third.

17. (*a*) Calculate the velocity of an electron which has been accelerated in an X-ray tube by a voltage of 100,000 volts. The rest mass of an electron is 9×10^{-28} g.

(*b*) Calculate the mass of the electron moving with this velocity using the formula given in Problem 4.

18. Calculate the wave lengths in angstroms of infrared bands which correspond to the Raman lines recorded at *a*, *b*, and *e* in Fig. 137*D*.

Some Raman lines appear in the Raman spectra which are not present in the infrared on account of restrictions which apply to the molecules in their ground state.

19. Calculate the necessary data, and plot a Morse curve for hydrobromic acid as shown in Fig. 141.

---

20. Calculate the Morse curve for bromine. With reference to equation 21 on page 588, $D' = 45.69$ kcal; $a = 1.98$, and $r_0 = 2.28$ A.

21. The vibrational frequency V of a simple harmonic oscillator is given by $V = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}}$, where f is the force of restitution on the vibrating particles and μ is the reduced mass of the system. For a "dumbbell-shaped" diatomic molecule $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$, where m_1 and m_2 are the masses of the individual atoms. The fundamental frequency of the HCl^{35} molecule occurs at 3.64μ. What would be the separation in angstroms between the fundamental vibrations for HCl^{35} and HCl^{37} if the forces of restitution are assumed the same in both cases? Between DCl^{35} and DCl^{37}? (The fundamental frequency of DCl^{35} is at 4.8μ.)

CHAPTER XX

PHOTOCHEMISTRY

Collisions between Molecules and Photons. Photochemistry comprises the study of chemical reactions produced directly or indirectly by means of radiation. It was shown on page 368 that molecular collision is the cause of ordinary chemical reactions. Only those molecules which contain an abnormal amount of energy can effect chemical reaction, and only a few molecules can obtain this energy from collision if the activation energy is large and the temperature is low. Reactions of this type are necessarily slow.

It is possible, however, to activate molecules with an external source of energy, as, for example, by introducing a beam of light having the proper frequency to be absorbed and a sufficient quantity of energy in each photon to effect the reaction. The underlying photochemical reactions induced by energy from an outside source is suggested in **Fig. 142.** The full line represents the distribution of energy among a group of molecules due to random collisions from heat, similar to that shown in Fig. 96 on page 368. The number of molecules with high energy (at the right) sufficient for chemical reaction is small. The dotted line represents the situation when a large number of energy-rich molecules are produced by introducing a beam of light of the proper frequency. It is clear that the intensity of light introduced does not depend on the temperature of the reaction vessel. Accordingly, the primary process of photoactivation has a very low temperature coefficient in contradistinction to the large temperature coefficient of thermal reactions. If the over-all photochemical reaction has a large

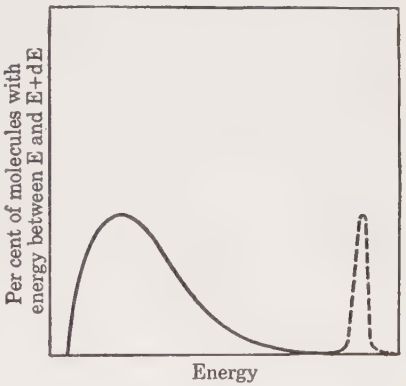


FIG. 142. Distribution of energy among molecules. The dotted line shows how the absorption of light from an external source can increase greatly the number of molecules of high energy and produce photochemical reactions.

temperature coefficient, it may be concluded that an ordinary thermal reaction is the rate-determining step.

A *photon* of radiation is a unit of radiation which possesses one quantum of radiation. Frequently, however, the term quantum is used interchangeably with the term photon.

When a photon of radiation comes close to a molecule, several different things may happen. If there is no possible electronic, atomic, or molecular change that can use the exact amount of energy contained in the photon of radiation, there will be no interaction and no chemical or physical change. However, if there is within the molecule some change which is not in conflict with the quantum restrictions and which corresponds to the energy of the photon, there may be a transfer of energy, and the photon is "absorbed." After a molecule has received this energy, it may give it up on collision with other molecules, thus increasing their kinetic energy. The total effect is thus a conversion of radiant energy into thermal energy and the raising of the temperature. This is the most common effect of the absorption of radiation.

The energy of a quantum may be transformed in several different ways summarized as follows:

1. *Heat.* The temperature of the absorbing system is raised.
2. *Dissociation.* The molecule undergoes a chemical breakdown.
3. *Excited molecule.* The molecule retains its energy until it can be used chemically (*a*) by combination with some other molecule or (*b*) by transferring its energy to another molecule which in turn utilizes the energy to produce chemical change.
4. *Dissociation and excitation.* One of the dissociated fragments is excited.
5. *Ionization.* The electron is driven out of the molecule leaving a positively charged ion.
6. *Fluorescence.* The excited molecule immediately reradiates part of the energy at a different wave length, as the electron returns to a lower energy level. If there is a time lag in this reradiation, the phenomenon is known as phosphorescence.
7. *Physical interaction.* The quantum of radiation is not absorbed and re-emitted, but rather it imparts some of its energy (*a*) to an electron as observed in the Compton effect or (*b*) to atomic or molecular action as observed in the Raman effect.

Types of Spectra. The absorption spectrum of a substance gives valuable information concerning the initial step, or the primary process, involved in any possible photochemical reaction. A molecule may be excited in several different ways, depending on the frequency of radiation absorbed. These different methods of absorbing radiation in the

different parts of the spectrum and the energies involved are summarized in **Fig. 143.**

In the upper half of the figure are given the general types of spectra together with the wave-length regions and the energy of the radiation in calories per mole. In the lower part is given a crude representation of what happens when the radiation is absorbed. The black dots represent electrons, and the larger circles represent atoms in the molecule. The same general considerations apply to polyatomic as well as to diatomic molecules. All the intramolecular changes involve definite energy increments which are governed by the quantum theory.

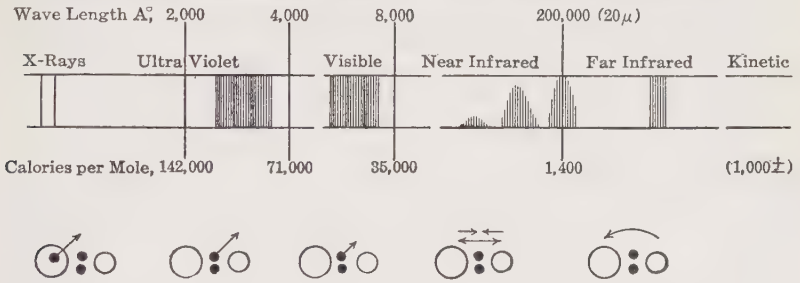


FIG. 143. Schematic representation of different types of spectra showing wave-length ranges and energy ranges in which they occur, and the corresponding electronic, vibrational, and rotational motions.

Absorption in the far infrared causes the molecule to rotate as indicated by the curved arrow at the right. The energy involved in these operations is of the order of a thousand calories per mole.

This is the only operation which can be carried out with energies of this magnitude, and so there are definite lines corresponding to quantum numbers. Absorption in the near infrared displaces atoms from their normal positions and causes them to oscillate back and forth or to move sidewise with a swinging motion within the molecule. These operations involve energies between about 1000 and 30,000 to 40,000 cal. The rotations, involving small energies, are superimposed on the atomic displacements, giving rise to absorption bands. The intramolecular changes can be combined so as to give harmonics absorbing approximately two or three or more times as much energy as the energy of the fundamental absorption band and causing absorption bands at roughly one-half and one-third the wave length. The probability of absorbing energy corresponding to two or three or more quanta is less than the probability of absorbing one, and so the fundamental band (the one-quantum operation) is the most prominent, and the absorption becomes progressively less intense at the higher harmonics. This

decrease in intensity at the shorter wave lengths is represented diagrammatically by reducing the height of the bands.

In the visible and ultraviolet region of the spectrum the absorption consists in displacing an outer electron in the molecule. The only difference between the ultraviolet and visible spectra is that greater energies and larger displacements are involved in the ultraviolet absorption—35,000 to 71,000 cal per mole being required for absorption in the visible region and 71,000 to several hundred thousand for absorption in the ultraviolet.

Sometimes the energy of the ultraviolet is sufficient not only to displace the electron within the molecule but also to drive it entirely out of the molecule, thus producing ionization. In the visible and ultraviolet regions of the spectrum series of bands may be obtained by combining the energies of the three quantum-restricted operations—electron displacement, atomic displacement, and molecular rotation.

In the X-ray region of very short wave lengths (about 1 A), the electrons deep inside the atom nearest the nucleus are displaced. Energies of millions of calories per mole are required for these displacements.

If the energies of radiation or of suitable projectiles, such as alpha particles, are increased to a still greater order of magnitude (around 10^{10} cal per mole), it is then possible to affect the nucleus of atoms and produce the transmutation of elements.

The various absorption spectra, produced by the displacements indicated in Fig. 143, are usually the same as the emission spectra produced when the electrons or atoms return to their normal positions, or when the molecules are caused to rotate by collisions or other means.

At the extreme right of Fig. 143 is given for comparison the order of magnitude of the average kinetic energy of molecular translation $\frac{3}{2}(RT)$, a few hundred calories.

It was emphasized on page 370 that although the average kinetic energy may be only a few hundred calories per mole there are, nevertheless, a few molecules which have much greater energies that are sufficient to account for ordinary chemical reactions.

The energies required for most chemical reactions range from about 10,000 to 100,000 cal. It is evident then that the longer infrared radiation is powerless to produce chemical reaction and that X rays contain so much energy that they are more likely to accomplish chemical reactions through secondary effects. Visible light and particularly ultraviolet light are, then, of chief interest in photochemistry.

Laws of Photochemistry. *Only that radiation which is absorbed can produce chemical change.* As Grotthus pointed out in 1818, there cannot be photochemical reaction unless the radiation is absorbed. However,

it does not follow that absorbed radiation must produce chemical reaction—more often it is converted into heat.

Einstein's law of photochemistry is important in the theoretical interpretation of photochemical reactions. According to this law, *in the primary photochemical process each molecule is activated by the absorption of one photon.*

In this simple primary process, then, we should find that the number of molecules activated is exactly equivalent to the number of quanta absorbed, and for a gram molecule of 6.02×10^{23} molecules there should be 6.02×10^{23} quanta absorbed. This "gram molecule" of quanta has been called the "einstein," just as a gram equivalent of electrons (6.02×10^{23} electrons or 96,500 coulombs) is called the faraday.

It must be strongly emphasized that the Einstein law is usually masked by secondary reactions and complicating circumstances which prevent a simple 1 to 1 relationship between the number of quanta absorbed and the number of molecules of *final* products in the reaction. Most investigators are inclined to accept the law as applied to the primary process and to look for the complicating circumstances which are peculiar to each particular reaction. Sometimes the activation process is followed by a simple stoichiometric reaction which gives some simple number, such as 2 molecules per quantum, or by a series of repeated reactions giving rise to a chain reaction. On the other hand, the activated molecules may be partially deactivated by collisions or by fluorescence or by internal rearrangements and loss as heat. Again, dissociated fragments resulting from the excitation may recombine so as to give low apparent yields. The quantum yield Φ is given by the expression

$$\Phi = \frac{\text{number of molecules reacting chemically}}{\text{number of quanta absorbed}} \tag{1}$$

The quantum yield provides a very convenient and significant means for describing the experimental facts and offers valuable information for drawing conclusions regarding the mechanism of the reaction.

It will be remembered that the energy in one quantum of radiation is given by the fundamental quantum relation:

$$\epsilon = h\nu \tag{2}$$

The energy per *einstein*, that is, per mole of photons, is obtained by multiplying this equation by the Avogadro number N:

$$N\epsilon = Nh\nu = 6.02 \times 10^{23} \times 6.62 \times 10^{-27}\nu \tag{3}$$

The frequency of radiation ν is related to the wave length λ and the velocity of light c (3×10^{10} cm/sec^{-1}) by the relation,

$$\nu = \frac{c}{\lambda} \tag{4}$$

Example 1. (*a*) Calculate the frequency of ultraviolet light, having a wave length of 3000 A.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{10}}{3000 \times 10^{-8}} = \frac{3.00 \times 10^{10}}{3 \times 10^{-5}} = 1 \times 10^{15}$$

(*b*) Calculate the wave length in centimeters and the wave number $\tilde{\nu}$ of light which has a wave length of 3000 A

$$3000 \text{ A} = 3000 \times 10^{-8} = 3.00 \times 10^{-5} \text{ cm}$$

$$\tilde{\nu} = \frac{1}{\lambda_{\text{cm}}} = \frac{1}{3.00 \times 10^{-5}} = 33{,}333 \text{ wave numbers}$$

(*c*) Calculate the energy in ergs per quantum and calories per "mole" in radiation of this frequency:

$$\epsilon = h\nu = 6.62 \times 10^{-27} \times 1 \times 10^{15} = 6.62 \times 10^{-12} \text{ erg per quantum}$$

$$Nh\nu = 3.98 \times 10^{12} \text{ ergs per mole} = \frac{3.98 \times 10^{12}}{4.184 \times 10^{7}} = 95{,}300 \text{ cal per mole}$$

(*d*) Calculate the energy in electron volts per molecule which corresponds to a wave length of 3000 A or an energy of 6.62×10^{-12} erg per quantum.

$$1 \text{ absolute electron volt} = 1.602 \times 10^{-12} \text{ erg}$$

$$\frac{6.62 \times 10^{-12}}{1.602 \times 10^{-12}} = 4.13 \text{ electron volts per molecule}$$

The energy associated with quanta of typical wave lengths is given in Table I.

The graphs given in **Figs. 144** and **145** are convenient for the conversion of radiation units.

In Fig. 144 kilocalories per mole are plotted against wave lengths in angstroms on the upper curved line and against frequencies ν or wave numbers $\tilde{\nu}$ on the upper straight line. For example, 4000 A intersects the kilocalorie curve at 71,000 (in agreement with Table I) and the volt curve at 3 volts. Again, a frequency ν of 12×10^{14} or a wave number of 40,000 corresponds to 116 kcal, or to 5 volts. It is possible to convert angstroms to frequencies or kilocalories to volts by shifting from one curve to the other. Thus, the intersection on ν of 12×10^{14} gives 116 kcal, and passing to the curve on the left 116 kcal corresponds to a little less than 2500 A.

TABLE I

Energy of Different Radiations

Wave Length, cm	Wave Number, $\tilde{\nu}$	Wave Length, A	Frequency, ν	Description	Energy of 1 quantum $h\nu$ in ergs	Energy of 1 einstein in cal per mole	Electron volts per electron
10^{-2}	10^{2}	1,000,000	3×10^{12}	Far infrared	1.99×10^{-14}	286	0.01
10^{-3}	10^{3}	100,000	3×10^{13}	Infrared	1.99×10^{-13}	2,860	0.12
10^{-4}	10^{4}	10,000	3×10^{14}	Near infrared	1.99×10^{-12}	28,600	1.24
8.0×10^{-5}	1.25×10^{4}	8,000	3.75×10^{14}	Edge of visible	2.48×10^{-12}	35,700	1.55
7.0×10^{-5}	1.43×10^{4}	7,000	4.29×10^{14}	Red	2.84×10^{-12}	40,900	1.77
6.0×10^{-5}	1.67×10^{4}	6,000	5.00×10^{14}	Yellow	3.31×10^{-12}	47,600	2.07
5.0×10^{-5}	2×10^{4}	5,000	6.00×10^{14}	Blue	3.95×10^{-12}	56,900	2.48
4.0×10^{-5}	2.50×10^{4}	4,000	7.5×10^{14}	Edge of visible	4.97×10^{-12}	71,500	3.10
3×10^{-5}	3.33×10^{4}	3,000	1×10^{15}	Ultraviolet	6.62×10^{-12}	95,300	4.14
2×10^{-5}	5.00×10^{4}	2,000	1.5×10^{15}	Ultraviolet	9.93×10^{-12}	143,000	6.20
1×10^{-5}	1×10^{5}	1,000	3×10^{15}	Ultraviolet	1.99×10^{-11}	286,000	12.4
1×10^{-8}	1×10^{8}	1	3×10^{18}	X rays	1.99×10^{-8}	2.86×10^{8}	12,400
1×10^{-9}	1×10^{9}	0.1	3×10^{19}	γ rays	1.99×10^{-7}	2.86×10^{9}	124,000
1×10^{-10}	1×10^{10}	0.01	3×10^{20}	γ rays	1.99×10^{-6}	2.86×10^{10}	1.24×10^{6}
1×10^{-11}	1×10^{11}	0.001	3×10^{21}		1.99×10^{-5}	2.86×10^{11}	12.4×10^{6}

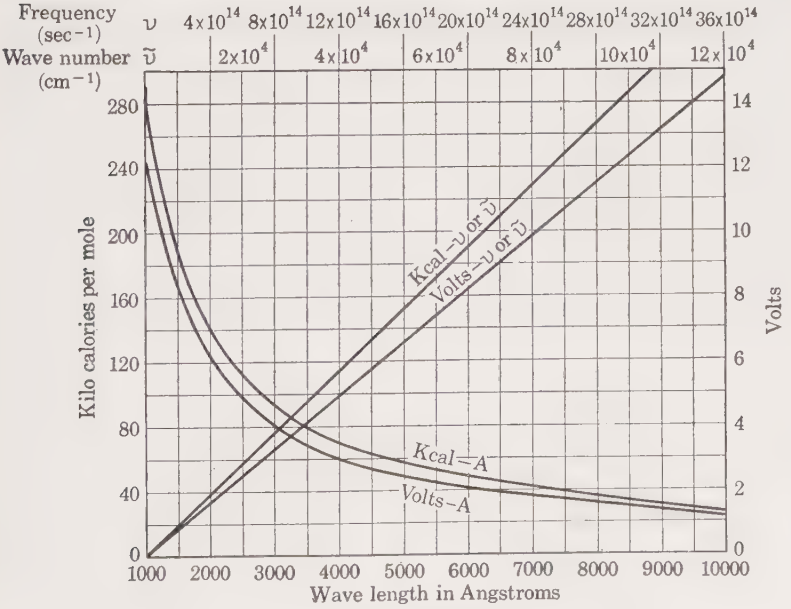


Fig. 144. Graphs for converting units of radiation into other units

The scale shown in Fig. 145 is useful for infrared spectroscopy. It enables one to convert wave lengths in angstroms or in microns directly into kilocalories, using the upper curve, or into wave numbers, using the lower curve.

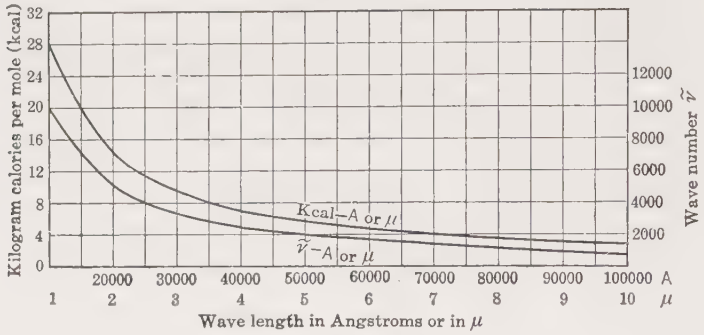


FIG. 145. Graphs for converting units of infrared radiation into other units.

Experimental Procedure.* In quantitative photochemical investigations it is usually important to use nearly monochromatic light of measured intensity.

The intensity of radiation is measured with a thermopile, which consists of a series of junctions of unlike metals, such as bismuth and silver or copper and constantan connected to a galvanometer. Alternate junctions are heated by exposure to the radiation, and the galvanometer deflections are proportional to the intensities of radiation. The junctions are covered with blackened metal strips of very low heat capacity, which convert radiation of all wave lengths directly into heat. The galvanometer readings may be converted into ergs of radiation per second per square millimeter striking the thermopile, by calibrating with a standard carbon-filament lamp from the U. S. Bureau of Standards.

The light can be restricted to a narrow range of wave lengths with the help of properly chosen filters which absorb the undesired wave lengths. The separation may be effected still better by refraction through a prism in a monochromator; the best results are obtained with a source of light like a mercury-vapor lamp which gives a discontinuous spectrum. Under these conditions a single spectral line may be isolated for the photochemical reaction. The intensity ob-

* Noyes and Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, 1941, Chapter II; Daniels, Mathews, and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1941; Daniels, *J. Phys. Chem.*, **42**, 701 (1938).

tainable with a monochromator is very low, and it is necessary to use capillary arcs or other very intense sources of light and to employ prisms and lenses of large dimensions in order to obtain sufficient intensity for investigating photochemical reactions. The reacting system is placed in glass or quartz vessels provided with clear polished windows, and the light is usually passed through the cell onto the thermopile. The actual energy absorbed in the reacting system is measured by subtracting these thermopile readings from those obtained when the cell is empty or filled with a transparent solvent. It is a still better plan to use two identical cells, one to contain the chemically reacting material and to act as a blank for obtaining the light intensity.

Failure to control the wave length and intensity may lead to erroneous conclusions. For example, when a certain reaction is exposed to sunlight through a red filter, it may proceed faster than when exposed through a blue filter. But red light is present in sunlight in much greater intensity than the blue, and one cannot conclude that the greater effect is due to the color; it may be due to the greater intensity. As another example, one may cite the action of the mercury-vapor lamp in producing ozone from oxygen. Ozone is synthesized by the short ultraviolet and decomposed by longer ultraviolet (2800 A). The actual yield of ozone depends then on the ratio of the intensities in these two regions, and this ratio depends on accidental conditions such as the age and the rate of cooling of the lamp. Experimental checks under such uncontrolled conditions cannot be expected.

In quantitative work where a knowledge of the reaction mechanism and rate is needed, it is not sufficient to place the reaction cell in front of a source of light. The reaction may slow down as the material is consumed not only on account of the decreased reaction rate but also on account of the lessened absorption of light. The number of calories of radiation or, better, the number of photons actually absorbed is the significant thing.

The amount of light absorbed in a given reaction cell will depend on the time of exposure, the concentration of the absorbing material, the thickness of the cell, and the intensity of the incident light. Instead of specifying all the variables it is much simpler to express the facts in terms of the number of molecules reacting per photon of radiation actually absorbed, that is, in terms of the quantum yield Φ.

Because the intensity of available monochromatic radiation is so low, it has been common practice to restrict quantitative photochemical studies to those reactions for which microanalytical methods are available or for which they can be developed.

The intensity of light available for photochemical reactions is measured most accurately with a thermopile, but with limitations it may sometimes be measured with a photoelectric cell or by the amount of photochemical reaction produced in an *actinometer*. It is necessary to calibrate these measuring devices against a thermopile. The blackened receivers of a thermopile are equally responsive to all wave lengths, whereas photoelectric cells and the actinometers do not necessarily give equal response for the same energy input at different wave lengths.

The uranyl oxalate actinometer, studied with great accuracy by Leighton and Forbes,* is the best for most purposes. Although the quantum efficiency changes slightly with the wave length, it may be taken that in a solution $M/100$ in UO_2SO_4 and $M/20$ in $H_2C_2O_4$, 0.57 molecule of the oxalic acid is decomposed for each quantum of light absorbed between the wave lengths 2540 and 4350 A. In other words, each mole of oxalic acid decomposed is equivalent to 1.75 einsteins, or to 166,000 cal, if an average wave length of 3000 A is assumed. The uranyl ion undergoes no chemical change.

For very low light intensities photoelectric cells and Geiger–Müller counters (page 625) are useful, but in photochemical work it is usually the sensitivity of the chemical tests rather than the sensitivity of the radiation measurement which limits the accuracy.

Photochemical Kinetics. The kinetics of photochemical reactions is more complicated than the kinetics of thermal reactions because more variables are involved. The intensity of light and the size and shape of the vessel may affect greatly the rate of the reaction. A photochemical reaction may be accompanied by a thermal reaction, identical with the photochemical reaction, or opposite to it, or entirely different in character. A photochemical reaction may produce a catalyst which then causes a thermal reaction to proceed at a measurable rate. Sometimes an *induction period* is necessary while a sufficient quantity of catalyst is being accumulated to make the reaction proceed with a measurable velocity. Again a thermal reaction once started may continue after the illumination is stopped, giving an *aftereffect*. The energy available in a photochemical reaction is much greater than in the thermal reaction, and this fact often changes the character of the reaction. For example, the thermal dissociation of hydrogen iodide at 450° is bimolecular ($2HI = H_2 + I_2$), but the photochemical reaction is unimolecular ($HI = H + I$) because the extra energy required to produce free atoms is available.

Not only second-order and first-order reactions but zero-order reactions also are found in photochemistry. A zero-order reaction is one in

* Leighton and Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930).

which the rate is entirely independent of the concentration. For example, if the concentration is high and the light intensity is weak, the light intensity may be the limiting factor in the reaction rate, and the concentration may be without influence on the rate.

If the reaction cell is short, the absorption of light is slight, so that practically all parts of the reacting system have about the same illumination, and stirring becomes unimportant. If, on the other hand, the light is largely absorbed in the first portion of the reacting system, the extent of the reaction will vary with the depth, and vigorous stirring may be necessary to give uniform and reproducible conditions, particularly in long cells.

If light causes a reaction in one direction, giving a zero-order reaction, and a thermal reaction occurs in the opposite direction proportional to the concentration of the photochemical product, a stationary state will eventually be produced in which the two rates are exactly equal. The situation is described mathematically by the following equation:

$$\frac{dx}{dt} = k_{\text{photo}}I - k_{\text{thermal}}x \tag{5}$$

where k_{photo} and k_{thermal} are the specific reaction rates of the photochemical and thermal reactions and x is the amount of material produced by the photochemical reaction. When a steady state is reached,

$$k_{\text{photo}}I = k_{\text{thermal}}x, \quad \text{and} \quad x = \frac{k_{\text{photo}}I}{k_{\text{thermal}}} \tag{6}$$

The concentration of material in the stationary state changes with the intensity of the light. An example of this type of reaction is the photopolymerization of anthracene, dissolved in xylene. In the presence of ultraviolet light this substance forms dianthracene which has twice the molecular weight of anthracene, but in the dark the dianthracene is depolymerized, giving the original anthracene.

The experimental determination of the quantum yield constitutes an excellent method for studying *chain reactions* (page 387). If several molecules of products are formed for each photon of light absorbed, the reaction is obviously a chain reaction in which the products of the reaction are able to activate additional molecules of reactants.

The photocombination of hydrogen and chlorine is a classical example of such a reaction, about a million molecules reacting for each quantum absorbed. Each molecule of hydrochloric acid formed undergoes further reaction with the hydrogen and chlorine atoms produced

(page 388). The measurement of the number of molecules per photon gives a measure of the average number of molecules involved in the chain.

In studying the kinetics of a photochemical reaction it is desirable to give the experimental facts by stating the quantum yield. For further information it is desirable to determine the influence of concentration and thus establish the order of the reaction, to determine the influence of temperature and thus ascertain whether or not thermal reactions are playing an important part, and to determine the influence of light intensity. If the quantum yield changes with the light intensity (that is, the amount of the reaction is not directly proportional to the intensity of light), it may be concluded that the light intensity is not the limiting factor or that more than one reacting molecule or fragment is produced by the light, each in turn taking part in secondary reactions.

Writing a rate equation for the photochemical reaction, including a term for the intensity of the light, describes most comprehensively the facts of a photochemical reaction. Although these expressions may be largely empirical, they frequently reveal much concerning the true mechanism of the reaction.

Example 2. The following reactions describe the photochemical decomposition of hydrogen bromide with light of 2530 A at 25°. The primary process disrupts the molecule into atoms of hydrogen and bromine which can then undergo further reactions. The quantum yield for the primary process is sometimes designated by ϕ, whereas the quantum yield for the over-all reaction is designated by Φ. The intensity of light absorbed is designated by I.

(1) $HBr + h\nu = H + Br$	Rate $= \phi I$
(2) $H + HBr = H_2 + Br$	Rate $= k_2 c_H c_{HBr}$
(3) $Br + Br + (M) = Br_2 + (M)$	Rate $= k_3 c_{Br}{}^2 c_M$
(4) $H + Br_2 = HBr + Br$	Rate $= k_4 c_H c_{Br_2}$

The over-all reaction is

$$2HBr = H_2 + Br_2$$

Reaction 3 describing the recombination of bromine atoms requires a collision with a wall or a third molecule M in order to dissipate the heat of combination and permit the two atoms to remain united.

Other reactions might be written on paper, such as $Br + HBr = Br_2 + H$ and $Br + H_2 = HBr + H$, but they involve breaking bonds which require so much energy for activation that they do not proceed at room temperature and may be neglected.

As the bromine accumulates, reaction 4 becomes important and reduces the quantum yield.

These facts can be summarized by the expression for the disappearance of hydrogen bromide:

$$\Phi = \phi + \phi \frac{1 - (k_4 c_{Br_2}/k_2 c_{HBr})}{1 + (k_4 c_{Br_2}/k_2 c_{HBr})}$$

When the concentration of bromine is zero at the beginning of the illumination or when mercury or other "acceptor" is added capable of removing the bromine chemically,

$$\Phi = 2\phi \cong 2$$

Photosensitization. Very often the molecules which absorb the light take part in the photochemical reaction only in an indirect manner and act merely as carriers of energy. One of the outstanding examples is that of mercury vapor, activated by the absorption of ultraviolet light of 2536.7 A which is emitted by a mercury-vapor lamp. The energy corresponding to this radiation is very large (112,000 cal), and it is more than the 102,400 cal necessary to dissociate hydrogen molecules. When mercury vapor is mixed with hydrogen and exposed to light from a mercury-vapor lamp, the chief reactions may be represented by the following equations, where Hg* represents an activated mercury atom:

$$Hg + h\nu = Hg^* \tag{7}$$

$$Hg^* + H_2 = Hg + 2H \tag{8}$$

The hydrogen is transparent to this radiation. The mercury acts as a photosensitizer, and the hydrogen atoms readily reduce metallic oxides, nitrous oxide, ethylene, carbon monoxide, and other materials. The excited mercury atoms decompose not only hydrogen but also ammonia and many different organic compounds.

The photodecomposition of oxalic acid, sensitized by uranyl ion, has already been referred to as a reproducible reaction suitable for use as an actinometer. The light is absorbed by the colored uranyl ion, and the energy is transferred to the colorless oxalic acid which then decomposes. The uranyl ion remains unchanged and can be used over and over again indefinitely as a sensitizer. It is probable that some kind of an "energy bridge," or loose chemical compound, or "complex" must be formed in order that this energy may be transferred. Supporting this view is the fact that the absorption of light is increased somewhat by adding colorless oxalic acid to a solution of uranyl ion. This change in absorption of light on mixing is one method by which chemical interaction of solutes (or gases) can be detected. Uranyl ion and light will not bring about chemical reaction in all substances even if the light energy is sufficient. Apparently the transfer of energy

during an ordinary instantaneous collision is not often possible; some kind of a loose or temporary chemical combination is helpful in giving favorable conditions for the transfer.

Typical Reactions. A few typical photochemical reactions * are summarized in Table II.

TABLE II

QUANTUM YIELDS IN PHOTOCHEMICAL REACTIONS AT ROOM TEMPERATURE

Reaction	Approximate Wave Length Region in angstroms	Approximate Φ
1. $2HI = H_2 + I_2$	3000–2800	2
2. $S_2O_8^{--} + H_2O = 2SO_4^{--} + 2H^+ + \frac{1}{2}O_2$	3000–2500	1
3. $C_{14}H_{10} \rightleftharpoons \frac{1}{2}(C_{14}H_{10})_2$	<3600	1–0
4. $2NO_2 \rightarrow 2NO + O_2$	4350	0
	4050	0.7
	3660	1.5 (2)
5. $CH_3CHO \rightarrow CO + CH_4 (+ C_2H_6 + H_2)$	3100	0.5
	2537	1
6. $(CH_3)_2CO \rightarrow CO + C_2H_6 (+ CH_4)$	<3300	0.2
7. Croton aldehyde	<3100	0.0
8. $NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$	2100	0.2
9. $H_2C_2O_4 (+ UO_2^{++}) \rightarrow CO + CO_2 + H_2O (+ UO_2^{++})$	4300–2500	0.5–0.6
10. $2NO_3^- \rightarrow 2NO_2^- + O_2$	3000–2500	0.01–0.3
11. $Cl_2 + H_2 \rightarrow 2HCl$	4000	10^5
12. $Br_2 + C_6H_5CH{=}CHCOOH \rightarrow C_6H_5C_2H_2Br_2COOH$	<5500	100–1
13. $C_2H_2 \rightarrow \frac{1}{n}(C_2H_2)_n$	2000	7
14. $CO + Cl_2 \rightarrow COCl_2$	4000–4360	1000

Reaction 1 is one of the most exact photochemical reactions, and it has the same value of Φ from 2800 to 3000 A, at low pressures and high pressures, in the liquid state or in solution in hexane. The primary process $HI + h\nu = H + I$ is followed by the thermal reactions $H + HI = H_2 + I$ and $I + I = I_2$, thus giving two molecules of HI decomposed for each photon absorbed. Reaction 2 has a quantum yield of unity. Reaction 3 has a quantum yield of unity initially, but the reverse

* Noyes and Leighton, "Photochemistry of Gases," Reinhold Publishing Corp., New York, 1941, Appendixes, pages 415-465; Daniels, *J. Phys. Chem.*, **41**, 713 (1938).

thermal reaction reduces it as the product accumulates. In reaction 4 at 3660 A the photoprocess is completely efficient ($\Phi = 2$) if correction is made for internal screening by the accompanying N_2O_4 which absorbs some light at 3660 A. The reactions are $NO_2 + h\nu = NO_2{}^*$, $NO_2{}^* + NO_2 = 2NO + O_2$ where the asterisk indicates an activated molecule. At longer wave lengths the spectrum is of a different type, and at 4350 A no reaction occurs when the radiation is absorbed.

Reaction 5 likewise shows a greater photochemical efficiency at the shorter wave lengths where the absorption spectrum is different. This reaction is interesting because at 300° Φ has a value of more than 300 indicating that the free radicals which are first produced by the absorption of light are able to propagate a chain reaction at the higher temperatures.

In reaction 6 the primary reaction is probably $CH_3COCH_3 + h\nu \rightleftharpoons CH_3 + COCH_3$. The acetyl radical can then decompose into CO and CH_3, or it can react with CH_3 to give back acetone. At room temperature it forms biacetyl $(COCH_3)_2$. In crotonaldehyde, reaction 7, no photochemical decomposition is observed.

In the photolysis of ammonia, reaction 8, hydrogen atoms are split off, and the low yield is probably due to partial recombination of the fragments. The quantum yield varies with pressure and reaches a maximum at 80–90 mm.

Reaction 9 illustrates a photosensitized reaction. Reaction 10 is complicated and depends on the pH of the solution. It is more efficient at the shorter wave lengths. Reaction 11 is the best-known example of a chain reaction, and it is one of the longest chains. Oxygen and certain other substances act as inhibitors by combining with the chlorine or hydrogen atoms, thus stopping the propagation of the chain and reducing the quantum yield.

The addition of bromine to cinnamic acid, reaction 12, is a chain reaction, the length of which depends on the temperature and the concentration of bromine and the amount of dissolved oxygen. The reaction can be split up into the primary photoprocess, which is not affected by temperature, and the subsequent thermal reaction which has a large temperature coefficient. When oxygen is removed, the breaking of chains is less frequent, and the quantum yield is of the order of hundreds and more.

The polymerization of acetylene, reaction 13, to give an insoluble substance called cuprene, is effected by short ultraviolet light with a quantum yield of about 7, showing that the primary process is followed by a short chain reaction.

Reaction 14 varies with the pressures of carbon monoxide and chlorine and, like all chain reactions, is sensitive to impurities.*

Luminescence. When a solid body, a bar of iron, for example, is heated to about 500°, it becomes "red hot"; when the temperature is raised still higher, it becomes "white hot," as the wave lengths of maximum intensity shift toward the shorter end of the spectrum in accordance with Wien's displacement law. It is possible, however, to produce light by other agencies than heat, and the radiation thus produced is called *luminescence* or sometimes "cold light." In all cases the emission of visible light may be attributed to the return of an outer electron toward its normal position after being displaced by kinetic bombardment of atoms and molecules, or by chemical or electric or other forms of energy.

Chemiluminescence is the emission of light by certain chemical reactions. Thus Evans and Dufford † have shown that the oxidation of ether solutions of magnesium *p*-bromophenyl bromide gives rise to marked chemiluminescence, the greenish-blue glow which accompanies the exposure of the solution to air being visible in daylight. The oxidation of decaying wood containing certain forms of bacteria, of luciferin in fireflies, and of yellow phosphorus are further examples.

Fluorescence is the emission of light by molecules or atoms which have been excited by the absorption of light, the fluorescent light having a wave length different from that of the incident radiation. In general, the wave length of the transformed radiation is greater than that of the incident radiation, indicating that, since the radiated light has a lesser amount of energy, the molecule has absorbed some energy. This relation, to which numerous exceptions have been found, was first enunciated by Stokes. When the incident radiation is cut off, fluorescence ceases.

Among the numerous substances which are known to exhibit the phenomenon of fluorescence may be mentioned fluorite (from which the phenomenon derived its name), uranium glass, petroleum, solutions of certain organic dyestuffs, eosin, fluorescein, quinine sulfate, chlorophyll, and the vapors of sodium, mercury, iodine, and acetone.

The characteristic fluorescence of various substances when exposed to the invisible ultraviolet light provides an effective means of analysis in many cases.‡ Moreover, the intensity of fluorescence can be used

* Further details of facts and theories for these and other photochemical reactions may be found in Noyes and Leighton, *loc. cit.*

† Evans and Dufford, *J. Am. Chem. Soc.*, **45**, 278 (1923).

‡ Radley and Grant, "Fluorescence Analysis in Ultraviolet Light," D. Van Nostrand Co., New York, 1933.

for quantitative analysis. For example, the concentration of riboflavin in chloroform is determined by this method. The fluorescence produced by X rays falling on a film of barium platinocyanide or other material is the principle of the fluoroscope used in X-ray diagnosis.

There are also many substances known which continue to emit light for some time after the external light stimulus is removed. This phenomenon is termed *phosphorescence*. The sulfides of the alkaline earths may be mentioned as examples of phosphorescent substances. A trace of one of the heavy metals greatly intensifies the light emitted by a phosphorescent substance. Usually impurities, in the form of mixed crystals, are necessary for phosphorescence. Many different colors are now available among the phosphorescent compounds.

Bombardment by electrons produces luminescence in rarefied gases at low pressures and in certain organic and inorganic crystals. The amount of visible fluorescence produced by a given input of energy may be large. This is the basis of the development of "fluorescent" lighting. Alpha particles from radioactive elements produce bright luminescence when they hit a screen of zinc sulfide. Luminescent paints for watch dials are made by mixing the zinc sulfide and the radioactive material together with a binder.

Considerable progress has been made in studying the effect of radiations on crystals. When X rays are passed through certain crystalline materials, characteristic colors are produced. Potassium chloride and quartz become blue. The color of irradiated alkali halides is probably due to absorption of light by electrons which have been released by X rays and trapped in negative-ion "vacancies" in the crystal lattice. This explanation involving vacancies in an imperfect lattice has been helpful in understanding other properties of the colored crystals such as thermal bleaching and photoconductivity, and in developing certain aspects of the theory of the photographic process.

Photography. If silver chloride or bromide is mixed with gelatine and given a very brief exposure to light, no change is observed; but, when it is immersed in a solution of a mild reducing agent, such, for example, as pyrogallic acid, the parts which have been exposed to light are developed; that is, they are reduced to metallic silver much more rapidly than the unexposed parts. The photographic plate consists of a large number of minute grains of crystalline silver halide; some of these grains are completely reduced by the developer to black metallic silver, and others are unaffected. Apparently, it is necessary for a quantum of energy to strike a sensitive spot in the crystal lattice in order that the silver halide may be reduced to give a nucleus of silver which then spreads, on further reduction, to include the whole

grain.* These sensitive spots seem to be identified with minute impurities of silver sulfide in the crystal lattice which are particularly responsive to the action of light. By increasing the number of these sensitive spots and by other means the speed of photographic films and plates has been greatly increased; that is, satisfactory photographs can be made with much weaker light than was possible heretofore.

The camera and lens focus the image of the object on the photographic plate; the brightest parts of the image have a greater concentration of photons, and, consequently, more grains are reduced to silver. The unaffected grains are dissolved out with sodium thiosulfate ("hypo") and the plate is washed and dried. The bright parts of the image become the dark spots on the plate, and the plate is therefore called a negative.

In printing, the plate is placed over a paper coated with silver halide and exposed to the light. The dark spots of silver on the negative absorb the light, whereas the unaffected areas permit light to pass through and act on the silver halide, producing a negative of the first negative. This double reversal produces a print in which the dark and light parts agree with the dark and light parts of the original object.

The silver halides respond only to the ultraviolet and to the shorter wave lengths of the visible spectrum, but, if certain red dyes, such as dicyanin, are mixed in the emulsion, the plate becomes sensitive also to red. Such red-sensitive plates are called panchromatic plates and give much better tone values to colored objects. This phenomenon constitutes another example of photosensitization. The red light is less scattered than the blue, and much clearer pictures of distant objects through a hazy atmosphere are obtained with red-sensitive plates using a color filter which absorbs the blue. This method is used in aerial photography.

Biological Applications of Photochemistry. The most important photochemical reaction in the world is the union of carbon dioxide and water in plants through the agency of sunlight and chlorophyll. Chlorophyll is a complex organic compound containing magnesium, which gives to plants their green color. It absorbs red and blue and, to a lesser extent, green light, as shown in Fig. 27 on page 82. The activated chlorophyll thus formed is responsible for the production of the starting material for all plant growth, utilizing carbon dioxide and water.

The important primary reaction involved in the growth of plants may be represented by the equation:

$$CO_2 + H_2O + h\nu + \text{chlorophyll} \rightarrow \frac{1}{n}(CH_2O)_n + O_2 + \text{chlorophyll} \quad (9)$$

* James and Kornfeld, *Chem. Rev.*, **30**, 1 (1942).

Now the reaction,

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad (10)$$

evolves 672,000 cal of heat, and the reverse reaction must absorb 672,000/6 or 112,000 cal per gram atom of carbon. The energy of activation required for reaction 9 must be at least as great as the endothermic heat of reaction (page 374). This energy of 112,000 cal per mole corresponds to a wave length of about 2300 A or less. Short ultraviolet light absorbed by carbon dioxide or water is known to bring about a reaction between carbon dioxide and water, but there is practically no radiation of this wave length in the sun's radiation that reaches the surface of the earth.

Chlorophyll, however, acts as a photosensitizer, absorbing visible light and making it available for photosynthesis in the plant. But there is something unique about the reaction. Photons of red light correspond to only 40,000 cal per mole, and yet they are able to do chemical work which demands at least 112,000 cal per mole. Obviously, nearly three or more photons must work together to bring about the reaction, but no other reaction has yet been observed in the laboratory where low-energy photons can add together in a single step to do a high-energy job of this kind.

It is likely that reaction 9 takes place in several steps, each requiring one quantum, and each leading to a further partial reduction of the carbon dioxide. Experiments on algae show that the quantum yield under the most favorable condition is about 0.1 molecule of carbon dioxide consumed or oxygen evolved per quantum,* corresponding to an efficiency with red light of about 28 per cent. Previously, it had been erroneously thought that the quantum yield was 0.25, corresponding to a much higher efficiency.

The reaction mechanisms are very complicated, but, by using radioactive carbon dioxide (page 663) as a tracer, it has been found that the first chemical intermediate produced in photosynthesis possess both a carboxyl group and a hydroxyl group. Some type of polymerization then may give rise to cellulose or related products. Intensive research on the mechanisms of this important reaction is now going on.†

Another photochemical reaction of biological importance is the production of vitamin D, which prevents rickets and brings about the normal deposition of calcium in growing bones. Steenbock found that rickets could be prevented by subjecting the food as well as the patient

* Manning, Stauffer, Duggar, and Daniels, *J. Am. Chem. Soc.*, **40**, 266 (1938).

† Symposium, American Association for the Advancement of Science, Chicago, Dec. 27 and 28, 1947.

to ultraviolet light below 3100 A. Later the substance which is converted into vitamin D was traced to ergosterol.

Example 3. When ergosterol is irradiated with ultraviolet light below 3100 A, vitamin D, the antirachitic vitamin, is produced in proportion to the number of quanta absorbed. When irradiated ergosterol was included in a diet otherwise devoid of vitamin D, it was found that absorbed radiant energy of about 750 ergs was necessary to prevent rickets in a rat when fed over a period of 2 weeks. The light used had a wave length of 2650 A.

(*a*) How many quanta are necessary to give 750 ergs?

$$\epsilon = h\nu = 6.62 \times 10^{-27} \times \frac{3.0 \times 10^{10}}{2.65 \times 10^{-5}} = 7.5 \times 10^{-12}$$

$$\text{Number of quanta} = \frac{750}{7.5 \times 10^{-12}} = 1.00 \times 10^{14}$$

(*b*) If we assume that the primary photoprocess is the only chemical reaction, how many molecules of vitamin D per day are necessary to prevent rickets in a rat?

$$\text{Molecules per day} = \frac{1.00 \times 10^{14}}{14} = 7.14 \times 10^{12}$$

(*c*) If vitamin D has a molecular weight of the same order of magnitude as ergosterol (382), how many grams of vitamin D per day are necessary to prevent rickets in a rat?

$$\text{Grams per day} = \frac{7.14 \times 10^{12}}{6.02 \times 10^{23}} \times 382 = 4.53 \times 10^{-9}$$

The first measurements of this type were made before the vitamin D had been isolated. After the vitamin was isolated in nearly pure form, it was found that 5×10^{-8} g per day was the minimum dosage required to prevent rickets in a rat. This value is in agreement with the quantity estimated from theoretical photochemistry at a time when the nature of the vitamin was still unknown.

Müller and others have established the fact that mutations, leading to new species, can be produced in plants and insects by radiation with X rays. Apparently, the cells which are responsible for hereditary influence cannot be affected by mechanical methods without injuring the cells, but occasionally they can be influenced by photons of X rays. Injuries may result from overexposure. Collisions between photons of X rays and effective parts of the cells are very rare and can be detected only by the extraordinary magnification occurring in the growth of an organism. It has been suggested that *some* of the naturally occurring mutations which are responsible for the spontaneous origin of species and biological evolution are produced by cosmic radiation and gamma rays from traces of radioactive material, both of which are similar to X rays.

REFERENCES

Noyes and Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, 1941.

Rollefson and Burton, "Photochemistry and the Mechanism of Reactions," Prentice-Hall, New York, 1939.

Style, "Photochemistry," E. P. Dutton & Co., New York, 1931.

Bonhoeffer and Harteck, "Grundlagen der Photochemie," Theodor Steinkopff, Dresden, 1933.

Daniels, "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1938, Chapter V.

Duggar, "Biological Effects of Radiation," McGraw-Hill Book Co., New York, 1936.

National Research Council, Report of the Committee on Photochemistry, *J. Phys. Chem.*, **32,** 480–575 (1928); **42,** 699–854 (1938).

James and Higgins, "Photographic Theory," John Wiley & Sons, New York, 1948.

PROBLEMS

1. (*a*) What is the energy per photon of violet light having a wave length of 4000 A?

(*b*) How many calories per mole are there in 1 einstein (6.023×10^{23} quanta) of this radiation? *Ans.* (*a*) 4.97×10^{-12} erg per quantum. (*b*) 71,500 cal.

2. The following calculations are made on a uranyl oxalate actinometer, on the assumption that the energy of all wave lengths between 2540 A and 4350 A is completely absorbed. The actinometer contains 20 ml of $M/20$ oxalic acid which also is $M/100$ with respect to uranyl sulfate. After 2 hours of exposure to ultraviolet light, the solution required 34 ml of $KMnO_4$ solution to titrate the undecomposed oxalic acid. The same volume, 20 ml, of unilluminated solution required 40 ml of the $KMnO_4$ solution. If the average energy of the quanta in this range may be taken as corresponding to a wave length of 3500 A, how many ergs were absorbed per second in this experiment? *Ans.* 124,000 ergs.

3. The photopolymerization of anthracene reaches a stationary state, owing to the thermal decomposition of the dianthracene. For the photoreaction the temperature coefficient r is 1.1, and for the thermal reaction r is 2.8 where r is defined as k_{t+10}/k_t.

Calculate the effect of a 10° rise in temperature on the amount of dianthracene formed when the photostationary state is reached. *Ans.* 60.7 per cent decrease.

4. A sample of gaseous acetone is irradiated with monochromatic light of a wave length of 3130 A. Light of this wave length decomposes the acetone according to the equation:

$$(CH_3)_2CO + h\nu \rightarrow C_2H_6 + CO$$

The reaction cell used has a volume of 59 ml. The acetone vapor absorbs 91.5 per cent of the incident energy. During the experiment the following data are obtained:

Temperature of reaction	= 56.7°
Initial pressure	= 766.3 mm
Final pressure	= 783.2 mm
Time of radiation	= 7 hours
Incident energy	= 48,100 ergs per second

How many molecules are decomposed per quantum of absorbed energy; that is, what is the quantum yield? *Ans.* 0.17 molecule per quantum.

5. According to the hypothesis of Franck, the molecules of the halogens dissociate into one normal atom and one excited atom. The wave length of the convergence limit in the spectrum of iodine is 4995 A.

(*a*) What is the energy of dissociation of iodine into one normal and one excited atom?

(*b*) The lowest excitation energy of the iodine atom is 0.94 volt. What is the energy corresponding to this excitation?

(*c*) Compute the heat of dissociation of the iodine molecule into two normal atoms, and compare it with the value obtained from thermochemical data, 34.5 kcal per mole. *Ans.* (*a*) 57.22. (*b*) 21.67. (*c*) 35.54 kcal.

6. How many calories of sunlight of average wave length, 6000 A, will be required to synthesize a kilogram of carbohydrate material (CH_2O) if 10 photons are required for every molecule of carbon dioxide utilized? *Ans.* 15,780 kcal.

---

7. A certain photochemical reaction requires an activation energy of 30,000 cal per mole. To what values does this correspond in the following units: (*a*) ergs per molecule, (*b*) frequency of light, (*c*) wave number, (*d*) wave length in angstroms, (*e*) electron volts.

8. If a reaction responds to both red and violet light, 7000 A and 4000 A, with an equal quantum efficiency, will there be more photochemical reaction per 100 cal of light in the red or in the blue? How much more?

9. The oxidation of rubrene ($C_{42}H_{28}$) is effected by oxygen at a wave length of 4360 A with a quantum efficiency of 1 molecule per quantum. How many calories of this light will be required to photo-oxidize 1 g of rubrene?

10. In the process of photosynthesis about 10 quanta of red light at 6200 A are required for the reaction of 1 molecule of carbon dioxide with 1 molecule of water, according to the reaction:

$$CO_2 + H_2O = (CH_2O) + O_2$$

The heat of combustion of a carbohydrate (CH_2O) evolves 112,000 cal of heat per carbon atom. Calculate the energy efficiency of the process, that is, the ratio of 112,000 to the number of calories of light absorbed per mole.

11. Chloroform is often kept in dark bottles to prevent photo-oxidation by air, giving phosgene which is poisonous. The quantum yield of the photo-oxidation has been reported to be about 100 molecules per photon with light of 4360 A. How many grams of chloroform will be photo-oxidized by 10 cal of this light?

12. For 900 seconds light of 4360 A was passed into a carbon tetrachloride solution containing bromine and cinnamic acid. The average energy absorbed was 19,190 ergs per second. Some of the bromine reacted to give cinnamic acid dibromide, and, in this experiment, the total bromine content decreased by 3.83×10^{19} molecules. (*a*) What was the quantum yield? (*b*) State whether or not a chain reaction was involved. (*c*) If a chain mechanism is involved, suggest suitable reactions which might explain the observed quantum yield.

13. A cold high-voltage mercury lamp is to be used for a certain photochemical reaction which responds to ultraviolet light of 2537 A. The chemical analysis of the product is sensitive to only 10^{-4} mole. The lamp consumes 200 watts and converts 5 per cent of the electric energy into radiation of which 80 per cent is at 2537 A. The amount of the light which gets into the monochromator and passes out of the rear slit is only 10 per cent of the total radiation of the lamp. Fifty per cent of this 2537 A radiation from the monochromator is absorbed in the reacting

system. The quantum yield is 0.4 molecule of product per quantum of light absorbed. How long an exposure must be given in this experiment if it is desired to measure the photochemical change with an accuracy of 1 per cent?

14. Discuss the economic possibilities of using photochemical reactions in industry for valuable products with electricity at 1 cent per kilowatt-hour. Assume that 5 per cent of the electric energy consumed by a quartz-mercury-vapor lamp goes into light, and 30 per cent of this is photochemically effective. How much will it cost to produce 1 lb (453 g) of an organic compound having a molecular weight of 100, if the average effective wave length is assumed to be 4000 A and the reaction has a quantum yield of 0.8 molecule per photon? How much will it cost if the reaction involves a chain reaction with a quantum yield of 100?

15. (*a*) How many calories per mole is equivalent in energy to 2 electron volts? A lead storage battery gives about 2 volts.

(*b*) How many calories per mole is equivalent to 100,000 volts? X rays have energies of about 100,000 volts.

(*c*) How many calories per mole is equivalent in energy to 20 million electron volts? Some cosmic rays have energies of about 20 million electron volts.

16. Ammonia is decomposed by ultraviolet light of 2000 A with a quantum yield of 0.14 molecule per photon absorbed. (*a*) How many joules of this light would be necessary to decompose 1 g of ammonia? (*b*) Offer a suggestion to explain this comparatively low quantum yield.

17. Nitrogen dioxide is decomposed photochemically by light of 4050 A with a quantum yield of 0.5 molecule per photon, according to the reaction:

$$2NO_2 \rightarrow 2NO + O_2$$

The thermal reaction runs in the reverse direction. When an enclosed sample of nitrogen dioxide is illuminated for a long period of time, the quantum yield decreases and approaches zero. Suggest a mechanism to explain these facts, and write the chemical equations.

18. Calculate the maximum possible theoretical yield in tons of carbohydrate material (H_2CO) which can be produced on a square mile of land by green plants or trees during a 100-day growing season. Similar calculations apply to algae growing in a square mile of lake or ocean. Assume that the sun's radiation averages 1.2 cal per square centimeter per minute for 10 hours per day and that one-half the area is covered by green leaves. Assume that one third of the radiation lies between 4000 and 6500 A, which is the range of the light absorbed by chlorophyl, and that the average wave length is 5500 A. Assume that the leaves are thick enough to absorb practically all of the light which strikes them. The quantum yield under the most favorable circumstances has been established experimentally as 0.1; that is, 10 photons with chlorophyl can produce one H_2CO unit from 1 molecule of carbon dioxide and 1 molecule of water. Criticize these several assumptions.

19. Two mechanisms have been proposed for the photochemical decomposition of NOCl:

$$\text{A}\begin{cases} NOCl + h\nu \rightarrow NO + Cl \\ Cl + NOCl \rightarrow NO + Cl_2 \end{cases} \quad \text{and} \quad \text{B}\begin{cases} NOCl + h\nu \rightarrow NOCl^* \\ NOCl^* + NOCl \rightarrow 2NO + Cl_2 \end{cases}$$

What quantum yield would be expected for each mechanism? Given the following experimental facts, state which mechanism is probably correct:

The range of wave lengths effective in decomposition lies between 3650 and 6400 A.

The substance NOCl possesses well-defined absorption bands above 2500 A, with no regions of continuous absorption.

The minimum dissociation energy required to give NO and Cl is 46,400 cal.

20. The photochemical reaction between bromine and hydrogen to give HBr using light of 5000 A has a quantum yield of zero below 150° and between 1 and 2 at higher temperatures. The quantum yield for the photochemical reaction between chlorine and hydrogen is about 10^5. Explain the difference in the behavior of bromine and chlorine.

21. The photochemical oxidation of phosgene, sensitized by chlorine, has been studied by Rollefson and Montgomery.* The over-all reaction is

$$2COCl_2 + O_2 = 2CO_2 + 2Cl_2$$

and the rate expression which gives the effect of the several variables is

$$\frac{dc_{CO_2}}{dt} = \frac{kI_0 c_{COCl_2}}{1 + k' c_{Cl_2}/c_{O_2}}$$

where I_0 is the intensity of the light. The quantum yield is about two molecules per quantum. Devise a series of chemical equations involving the existence of the free radicals ClO and COCl which will give a mechanism consistent with the rate expression.

* Rollefson and Montgomery, *J. Am. Chem. Soc.*, **55**, 142, 4025 (1932).

CHAPTER XXI

ATOMIC AND NUCLEAR STRUCTURE

The atom consists of a central nucleus of very small dimensions, approximately 10^{-12} cm, in which is concentrated most of its mass, surrounded by electrons which give a total diameter of approximately 10^{-8} cm. The nucleus itself consists of neutrons and positively charged protons. The number of external electrons is equal to the number of protons in the nucleus, and this number, called the atomic number, determines the chemical behavior of the element. When the elements are arranged in order of increasing atomic number, they often fall into groups which have similar chemical properties. The weight of the atom depends on the sum of the weights of the protons and neutrons in the nucleus.

The nucleus remains unchanged during all ordinary reactions, and it is only the arrangement of electrons outside of the nucleus which is of interest in ordinary chemistry, where activation energies up to 100,000 cal per mole are sufficient for most reactions. The nucleus itself can be disintegrated, however, with much higher energies of a billion calories and more. Again, some of the elements possess unstable nuclei and undergo spontaneous change into other elements; that is, they undergo radioactive decay.

Conductance of Electricity through Gases. Experiments on the conductance of electricity through gases were carried out largely by J. J. Thomson and others in the English laboratories during the latter part of the past century. Their observations laid an experimental foundation on which much of our information regarding the structure of the atom and the structure of the nucleus is built. When two metal electrodes are placed in a glass vessel containing gas at atmospheric pressure, it is necessary to apply a potential of some 40,000 volts per centimeter before any appreciable amount of current will pass through the gas. Under these conditions a spark is produced. If the pressure of the gas is reduced progressively, the spark becomes more uniform and broadens out. When the pressure is decreased to about 0.5 mm, the negative electrode, or the cathode, appears to be surrounded by a luminous layer, and between this and the anode is a series of luminous stria-

tions separated by dark regions, the number of which depends on the pressure, the kind of gas, and the dimensions of the vessel.

The current is carried between the electrodes partly by electrons and partly by gas ions. Positive gas ions are produced when molecules have one or more of their outer electrons removed, and negative ions are produced when the electrons become attached to other molecules. Gas ions, then, are similar to electrolytic ions, which have been studied in earlier chapters, but they are not governed by the usual valence rules. Mercury vapor, for example, can exist with 0, 1, 2, 3, 4, etc., charges. Furthermore, the electrolytic ions are present before the passage of the electric current, but the gas ions are produced chiefly by the current itself, the few original electrons and ions acquiring sufficient velocity in the electric field to collide with neutral molecules dislodging electrons from them and producing many more ions. The dark spaces in the discharge tube indicate the regions where the electrons have not yet developed sufficient kinetic energy to ionize or excite molecules. Light is produced when ions are discharged and electrons return toward their normal positions of lower energy level. As the pressure is further reduced, the luminous columns change in appearance, and below 0.01 mm they disappear, and the glass wall opposite the cathode becomes luminescent. The color of this luminescence depends on the nature of the glass. It is produced by bombardment of the glass by negative particles or electrons driven out from the cathode.

It was found that an opaque object placed in the path of the cathode rays casts a shadow and that the rays travel in straight lines from the cathode. A small paddle wheel was made to revolve by the cathode rays, thus showing that the rays possess mechanical energy. If a concave cathode is used, the rays can be focused on a piece of platinum or other material so as to produce incandescence, thus showing that the rays possess considerable energy which can be converted into heat. These cathode rays or electrons were found to penetrate very thin sheets of aluminum and other materials, the extent of the penetration depending on the density of the absorbing material and on the applied voltage. The electrical nature of these cathode rays was demonstrated by the fact that they were deflected in an electrostatic field toward the positive electrode, thus indicating a negative charge. Again, when a magnetic field was applied, they were deflected in a direction which indicated that negative charges were moving away from the cathode.

Electrons. The experiments with cathode rays described in the preceding section were followed by quantitative measurements of these negative particles or electrons which are now known to be the fundamental units of electricity and which play a large part in the structure

of atoms and in chemical reactions. The determination of the ratio of charge to mass of the electron, the charge of the electron, and the mass of the electron will be outlined briefly.

In an evacuated tube shown in **Fig. 146** electrons are emitted from the negatively charged cathode C and attracted to the positively charged anode A, which has a small hole in it. The beam of electrons passing through this hole is rendered still sharper by passing through holes in several screens which are carefully aligned, so that a sharply defined fluorescent spot of light F is produced on the glass scale S. A magnetic

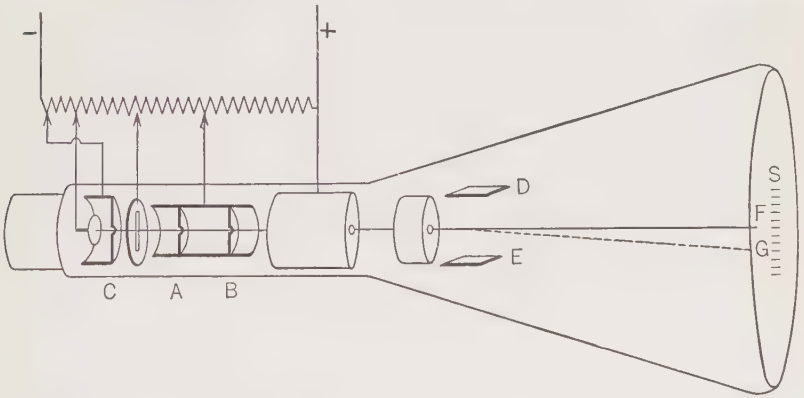


Fig. 146. Apparatus for measuring the ratio of mass to charge for an electron.

field H, not indicated in the figure, is applied of such strength that the spot of light moves down the scale to G. The force pulling it down is equal to Hev where e is the charge and v the velocity of the electron. There is a centrifugal force equal to mv^2/r where r is the radius of curvature of the deflected beam, tending to return the electrons to a straight path hitting the scale at F. As long as the spot of light stays at G, the two forces are equal, and

$$Hev = \frac{mv^2}{r} \tag{1}$$

Then

$$Hr = \frac{mv}{e} \tag{2}$$

An electrostatic potential E is now applied to the electrodes D and E which is just sufficient to return the spot of light to F. Then

$$Ee = Hev \tag{3}$$

and

$$v = \frac{E}{H} \tag{4}$$

Both E and H are measured experimentally, and, thus, the velocity v can be determined. It is 6×10^9 cm per second when the potential difference between A and C is 10,000 volts. If the value of v is substituted into equation 2, it is possible to obtain the ratio m/e. At low velocities it is 5.684×10^{-8} g per electromagnetic unit, and at higher velocities approaching the velocity of light the mass increases and approaches infinity, as predicted by the theory of relativity.

The charge on the electron was determined in the classic oil drop apparatus of Millikan * shown in **Fig. 147.**

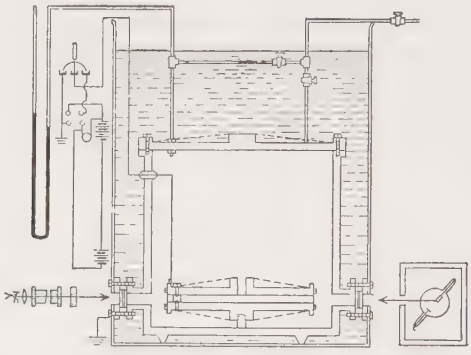


FIG. 147. Millikan's apparatus for measuring the charge of the electron.

A tiny droplet of oil is blown into a quiet thermostated air space between two electrodes, and its rate of fall is carefully determined with a microscope and scale. The surrounding air is then ionized with an X-ray beam, and a potential is applied. The oil drop picks up electric charges by colliding with ionized molecules of oxygen or nitrogen and moves more rapidly. The potential can be reversed, thus reversing the direction of the movement of the oil droplet. Since the speed of the movement is proportional to the number of charges, it is possible to calculate the magnitude of the charge by comparing the changes in velocity of the drop with the velocity when falling under the influence of gravity alone.

Millikan observed that several different charges were quite commonly acquired by a single drop, but in every case the total charge was invariably an exact integral multiple of an elemental charge e. The value of e obtained in this way and corrected for recent measurements on the viscosity of air is 1.602×10^{-19} coulomb or 1.602×10^{-20} electromagnetic unit.

X Rays and Atomic Numbers. In 1895 Roentgen found that a covered photographic plate was affected when placed near a tube in which

* Millikan, *Phys. Rev.*, **39**, 349 (1911); **2**, 109 (1913).

cathode rays were generated. The bombardment of the cathode rays on the walls produced radiation which he called "X rays"; this radiation was able to pass through objects which were opaque to ordinary light and act on photographic plates or produce fluorescence in certain crystals. These X rays were not deflected by an electrostatic nor an electromagnetic field and were, in fact, light rays of very short wave length.

Moseley placed different elements as targets in an X-ray tube and determined the wave length of the X rays, using a crystal as a reflection grating (page 48). As the atomic weight of the element increased, the wave length of the X rays decreased. The X-ray spectrum was quite simple, involving two lines, close together. In the heavier elements a second series of characteristic X-ray lines was found, and these too became displaced in the direction of shorter wave lengths as the atomic weight increased. In the heaviest elements a third series of X-ray lines was found. These three series are known as the K, L, and M series, respectively, and the doublets are designated as alpha and beta lines. Moseley arranged the elements in increasing atomic weights, starting with hydrogen and counting the elements 1, 2, 3, 4, etc., as they occur in the periodic table. The frequencies ν of the X rays were calculated by dividing the wave lengths of the X rays in centimeters into the velocity of light. When Moseley plotted the square root of these frequencies against the atomic number Z of the elements, he found that approximately straight lines were produced, as shown in **Fig. 148.**

Expressed mathematically,

$$\sqrt{\nu} = \text{constant} \times Z \qquad (5)$$

This *atomic number* Z is a fundamental constant. It is equal to the positive charge on the nucleus of the atom which in turn is the same as the number of electrons surrounding the nucleus in the uncharged atom.

The arrangement of elements according to their atomic numbers straightened out certain anomalies in the periodic table. Potassium follows argon, nickel follows cobalt, and iodine follows tellurium, in spite of the fact that classification by atomic weights puts them in the reverse order. The existence of nuclei with different weights but the same atomic number explains why this order is reversed and shows that the atomic number is a more fundamental property than the atomic weight. When Moseley prepared his table of atomic numbers in 1914, there were six gaps corresponding to six missing elements, but all of these have since been filled. Before the discovery of Moseley's relation there was doubt concerning the number of rare earth elements because

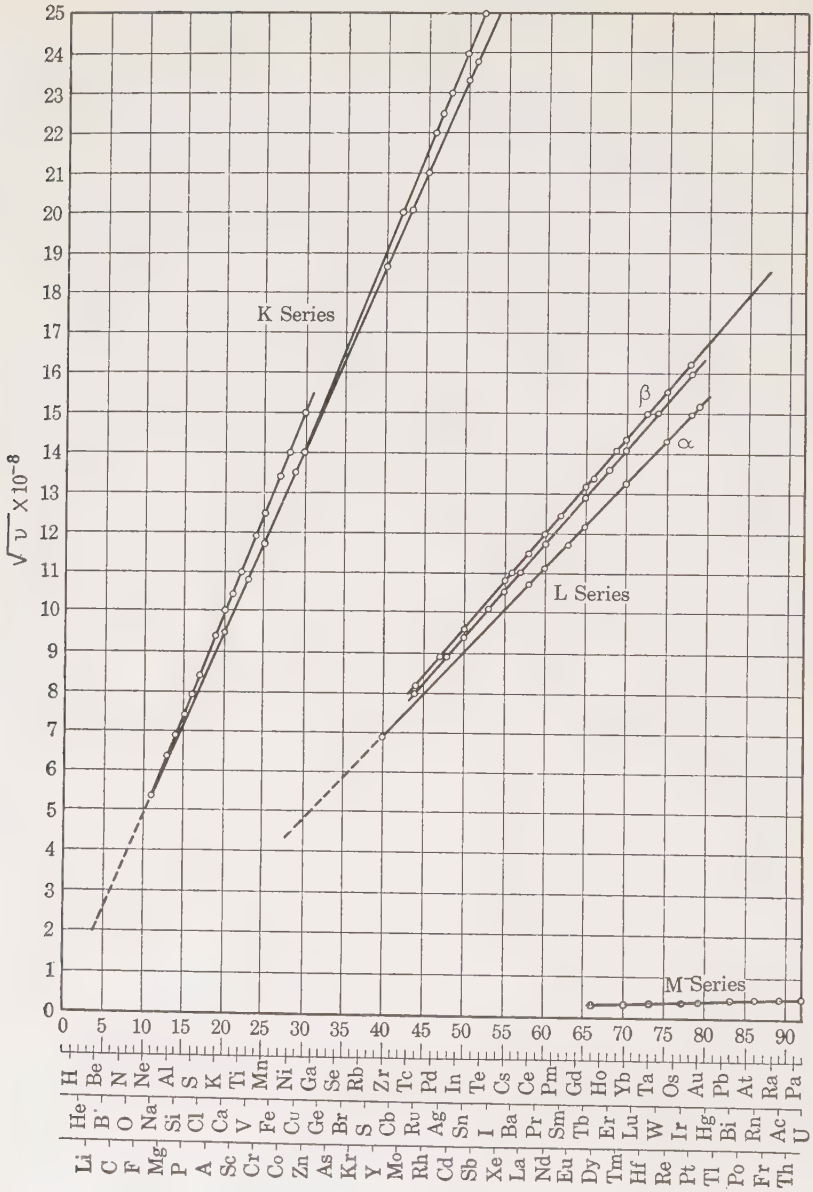

$\sqrt{\nu} \times 10^{-8}$
K Series
L Series
M Series
α
β
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90
H He Li Be B C N O F Ne Na Mg Al Si P S Cl A K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr Rb Y Zr Cb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe Cs Ba La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Ta W Hf Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn Fr Ra Ac Th Pa U

FIG. 148. Relation of atomic numbers of the elements to the frequencies of the X rays emitted.

the chemistry of these elements is so much alike. By referring to the graph of Fig. 148 it was found that, to make the line continuous, there should be 14 rare earth elements; also a homologue of zirconium between barium and tantalum. Thirteen of these positions could be filled from rare earth metals then known, and the homologue of zirconium was found later by Coster and Hevesy and called hafnium.

The Discovery of Radium. Following Roentgen's discovery of X rays, Becquerel studied the action of a number of fluorescent substances on a covered photographic plate. He had considered the possibility that those crystals which exhibited fluorescence under the action of X rays might emit X rays when caused to fluoresce by exposure to sunlight. Among the materials with which Becquerel experimented were salts of uranium and he found that a photographic plate brought near a fluorescent uranium salt was darkened by subsequent development, even though the photographic plate had been protected by an opaque cover. In carrying out a proper control experiment he was surprised to find that exposure to sunlight with the attendant fluorescence was not necessary for the action on the photographic plate. Furthermore, uranous and uranic salts both gave similar photographic action, in spite of the fact that the uranous salts were not fluorescent. Here, then, was the discovery of a spontaneous emission from some substances of penetrating rays similar to X rays. The phenomenon was called radioactivity.

In a classic investigation Professor and Madame Curie carried out a systematic examination of uranium minerals and found that one of them, pitchblende, was considerably more radioactive than uranium itself. With this clue they separated from tons of pitchblende a trace of a substance which possessed great radioactivity. After extensive chemical purification and a great many recrystallizations Professor and Madame Curie discovered the element radium.

Alpha, Beta, and Gamma Rays. The radiations emitted by the radioactive elements are of three kinds. The alpha particles have a mass equal to that of the helium atom and are shot out with a velocity about one-tenth that of light. They have a positive charge of two units and are deflected slightly in an electrostatic or magnetic field. They possess great ionizing power but relatively little penetrating power—only a few centimeters in air at atmospheric pressure. The beta rays consist of negatively charged particles moving with speeds varying from nine tenths of the speed of light to much lower velocities. Whereas the alpha particles emitted by a particular radioelement have a definite velocity, the corresponding beta-ray emission consists of a flight of particles having widely different speeds. The penetrating power of the beta rays is

conditioned by the speed of the particles, those which move most rapidly possessing the greatest penetrating power. The ionizing action of the beta rays is weaker than that of the alpha rays per unit length of path, but the total number of ions produced by an alpha particle and a beta particle of the same energy is about the same. The beta rays are greatly deflected by an electrostatic or magnetic field. The gamma rays consist of electromagnetic radiations like X rays, except that they come from the nucleus, whereas the X rays come from electron displacements outside the nucleus. Obviously, gamma rays cannot be deflected from a rectilinear path by either electric or magnetic fields. The relative penetrating power of the three rays are roughly in the order 1, 100, and 10,000 for the alpha, beta, and gamma rays.

When a current of air is passed through a solution of a radium salt, a small volume of a very radioactive gas is obtained. With the help of an extremely sensitive microbalance it was found to have an atomic weight of 222. This fact and the chemical inertness of the gas showed that it belonged to the group of rare gases of the zero group in the periodic table. It was given the name *radon.*

Direct proof of the nature of alpha rays was obtained by an experiment in which a very thin glass bulb was filled with radon and some radium and then enclosed in an outer glass tube with suitable windows. The outer tube was evacuated and allowed to stand. After several days the spectrum of helium was observed in the outer vessel when an electric discharge was applied. In a control experiment the inner bulb was filled with pure helium under pressure, but no trace of helium gas could be detected spectroscopically. These experiments showed that the helium as such could not go through the thin glass walls, but that the alpha particles were able to penetrate the walls and after losing their velocities became helium atoms. The nuclear reaction for this process is:

$$\mathrm{Ra} \rightarrow \mathrm{Rn} + \mathrm{He}$$

The atomic weight of the original radium is 226, the atomic weight of radon is 222, and that of helium is 4.

Measurement of Radioactivity. Action on a photographic plate through opaque paper constitutes one of the simplest qualitative tests for the radioactivity of a substance. This method can be used to reveal the distribution of a radioactive substance within an object, such as a mineral or a leaf.

Some materials such as zinc sulfide become luminous when exposed to radiation from a radioactive material, and the intensity of this radioluminescence is roughly proportional to the radioactivity. When examined with a lens, the luminescence is seen to consist of a series of

scintillations caused by the bombardment of alpha particles on the zinc sulfide. Practical use of this phenomenon is made in luminous paints, which are used, for example, on watch dials. A low-grade material of feeble radioactivity is mixed intimately with zinc sulfide, and the resulting scintillations are so frequent as to produce a uniform glow to the unaided eye.

A quantitative measure of radioactivity is obtained with ionization chambers. The radioactive material sends out radiations which ionize the surrounding gas, and, when an electrostatic field of the proper voltage is applied, the resulting current is a measure of the number of ions produced, which, in turn, is a measure of the radioactivity for a given species. The current is measured by means of an electrometer, or an electron-tube circuit. The most sensitive instrument is the Geiger–Müller counter, which can detect individual ionizing particles. It consists of a wire in the center of a metal cylinder enclosed in a tube with a suitable gas. The wire is maintained at a potential several hundred volts positive to the cylinder, and the entrance of an ionizing particle produces a momentary flow of current, multiplied by ionic collisions, which is amplified and caused to operate a counting dial.

The Wilson cloud chamber provides important means for studying ionizing rays. The paths of individual alpha or beta particles or ejected electrons are rendered visible by shooting the particles into a chamber containing supersaturated water vapor. Each alpha particle produces about 100,000 gas ions, and each of these ions condenses a droplet of water. The alpha particles travel in straight lines and leave behind them a wake of water droplets which are illustrated schematically in **Fig. 149.**

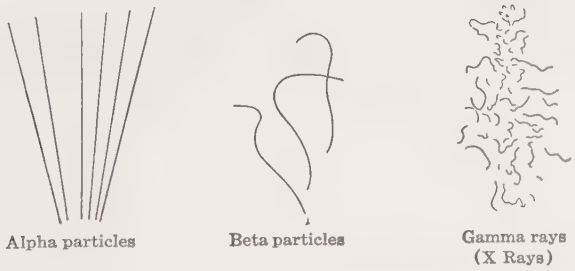


FIG. 149. Cloud tracks showing alpha, beta, and gamma rays.

Beta rays are more easily deflected, and their paths are quite crooked. Gamma rays or X rays release a large number of secondary electrons from the molecules which they strike. The energy of these secondary electrons is lower, and the paths are short and crooked. A photograph of alpha-particle tracks is shown in Fig. 156 on page 641.

Avogadro's Constant. Since it has been proved that each alpha particle is transformed into a helium atom and since we can count the alpha particles and measure the volume of helium, we have at once a direct method for determining the number of molecules in a gram molecule of helium, and this number is called the *Avogadro constant.*

Example 1. Rutherford and Geiger found that radium emits 3.4×10^{10} alpha particles per gram per second. Rutherford and Boltwood found that radium produces helium at the rate of 1.07×10^{-4} ml per gram per day, measured under standard conditions. What is the value of the Avogadro constant?

$$\frac{22{,}400}{1.07 \times 10^{-4}} \times 3.4 \times 10^{10} \times 24 \times 60 \times 60 = 6.15 \times 10^{23}$$

The direct counting of alpha particles combined with a measurement of the total charge of electricity carried by a large number of alpha particles gave a value of 3.1×10^{-19} coulomb. Deflection in an electrostatic field was in the direction which showed that the charge was positive. Since the fundamental unit of electricity (the charge on the electron) is 1.602×10^{-19} coulomb, the alpha particle must carry two positive charges.

The measurement of the charge on the electron gives a more accurate method for calculating Avogadro's constant.

Example 2. The charge on the electron is 1.602×10^{-19} coulomb. When water is electrolyzed, each electron releases an atom of hydrogen at the cathode, and 96,496 coulombs release 1.0076 g of hydrogen ions. What is the Avogadro number?

For hydrogen ions,

$$\frac{m}{e} = \frac{1.0076 \text{ g}}{96{,}496 \text{ coulombs}} = 1.044 \times 10^{-5} \text{ g coulomb}^{-1}$$

Since the charge on the hydrogen ion is the same as that of the electron,

$$m = 1.0449 \times 10^{-5} \times 1.602 \times 10^{-19} = 1.6739 \times 10^{-24} \text{ g}$$

The Avogadro constant, the number of atoms in a gram atom or ions in a gram ion, then, is

$$\frac{1.0073}{1.6739 \times 10^{-24}} = 6.025 \times 10^{23}$$

After the weight of a single atom of hydrogen has been established, the weight in grams of a single atom of any other element may be determined by dividing its atomic weight by 6.02×10^{23}.

The mass of the individual electron can be determined also. On page 620 it was shown that m/e for the electron is 5.684×10^{-9} g per

coulomb; for hydrogen it is 1.044×10^{-5}. Then

$$\frac{\frac{m}{e}\text{ (hydrogen ion)}}{\frac{m}{e}\text{ (electron)}} = \frac{1.044 \times 10^{-5}}{5.684 \times 10^{-9}} = 1837$$

Since the charges are equal, the mass of the electron must be 1/1837 the mass of the hydrogen ion. Inasmuch as the weight of the latter is 1.0073, the weight of the electron on the atomic weight scale is 0.000549.

Disintegration of the Radioelements. Most of the elements with atomic numbers greater than that of lead, 82, are unstable and undergo radioactive disintegration into lighter elements. This involves changes in the nuclei of the atoms, whereas ordinary chemical reactions involve changes only in the arrangement of atoms in molecules. The nuclear changes have energies of the order of 10^9 cal per mole and more, whereas molecular changes require energies of only 10^4 to 10^5 cal per mole. The energies involved in nuclear disintegrations are so great that the slight increases in energy produced by raising the temperature are entirely negligible, and, as a result, no detectable change in the rate of radioactive disintegrations has been observed in studies extending from liquid air temperatures to 1000°.

Again the radioactivity of an element is unaffected by chemical combination with other elements.

It will be shown presently that radioactivity is not confined to the heavy elements; in fact, radioactivity has been produced in most of the elements.

In all radioactive disintegrations the number of atoms disintegrating is proportional to the number present; and so radioactive decay always follows the first-order equation:

$$-\frac{dn}{dt} = kn \tag{6}$$

and the number n of atoms (or gram atoms) remaining unchanged after time t is given by the expression,

$$k = \frac{2.303}{t} \log \frac{n_0}{n} \tag{7}$$

where n_0 is the number at the beginning, when $t = 0$. The exponential expressions are used more commonly than the logarithmic for studying radioactivity. Thus:

$$n = n_0 e^{-kt} \tag{8}$$

When one radioactive element disintegrates, another may be formed, and the disintegration constant of the second radioelement is usually different from that of the first one. A series of consecutive first-order decompositions results which can be handled by the methods of differential equations, as illustrated on page 357. Radon is produced continuously by the disintegration of radium; and radon immediately disintegrates into another radioelement, radium A. The rate at which radon is produced from a quantity of radium is given by the expression $k_1 n_1$, where n_1 is the number of radium atoms, and k_1 is the disintegration constant of radium or the fraction disintegrating per unit of time; the rate at which it decomposes is given by the expression $k_2 n_2$, where n_2 is the number of radon atoms and k_2 is the disintegration constant of radon. When the rate of production of a radioelement from its parent element is equal to its rate of disintegration into the next succeeding element of the series, the substance is said to be in radioactive equilibrium. Under equilibrium conditions, radon is decomposing at the same rate that it is being formed, and

$$k_1 n_1 = k_2 n_2$$

Then, at equilibrium,

$$\frac{n_1}{n_2} = \frac{k_2}{k_1} = \frac{t_{\frac{1}{2},1}}{t_{\frac{1}{2},2}} \tag{9}$$

where $t_{\frac{1}{2}}$ is the period of half-life or $0.693/k$.

If the life of the parent element is long compared with the life of the disintegration products, and if sufficient time is allowed for equilibrium to be attained, the ratio of the quantities of successive radioelements is the same as the ratio of their half-lives. It is evident that the short-lived elements cannot accumulate in large quantities, but because of their rapid disintegration they may contribute largely to the radioactivity of the total material.

Example 3. Radium loses an alpha particle and leaves a gaseous element, radon. For the radio disintegration of radium, $t_{\frac{1}{2}} = 1590$ years and for radon $t_{\frac{1}{2}} = 3.82$ days. How many milliliters of radon at 25° and 1 atm are in equilibrium with 1 g of radium?

$$1 \text{ g radium} = \tfrac{1}{226} = 0.00442 \text{ gram atom}$$

$$\frac{n_{\text{Ra}}}{n_{\text{Rn}}} = \frac{t_{\frac{1}{2},\text{Ra}}}{t_{\frac{1}{2},\text{Rn}}}$$

$$\frac{0.00442}{n_{\text{Rn}}} = \frac{1590 \times 365.25}{3.82}$$

$$n_{\text{Rn}} = 2.87 \times 10^{-8} \text{ gram atom}$$

$$\text{Volume radon} = 2.87 \times 10^{-8} \times 22{,}412 \times \frac{298.1}{273.1} = 7.06 \times 10^{-4} \text{ ml}$$

When a short-lived radio element is removed from its long-lived parent, a new supply of the daughter element is regenerated, rapidly at first and then more slowly as the rate of decay of the daughter element increases, owing to the presence of the larger quantity which has accumulated. Thus, when gaseous radon is pumped or swept out of a solution of a radium salt with a current of air, the radium loses some of the short-lived beta and gamma radioactivity but regains it as the radon and its further decay products are allowed to accumulate again. If the decay of the daughter element is given by equation 8, the accumulation of the daughter element and the recovery of the original activity is given by the equation:

$$n = n_0(1 - e^{-kt}) \tag{10}$$

There are several radioactive decay series, three of which are shown in **Fig. 150.** The atomic numbers are given at the right in each series.

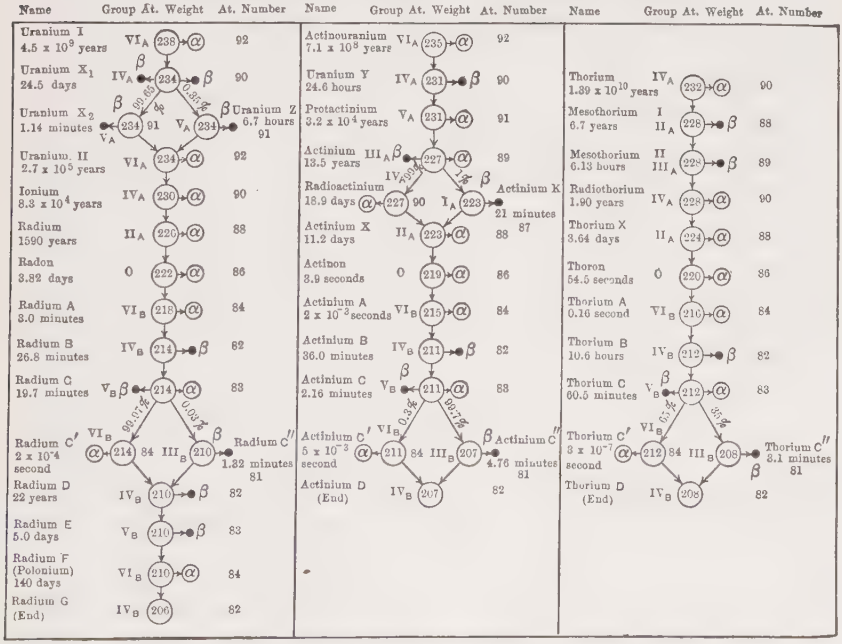


FIG. 150. Disintegration series of the naturally radioactive heavy elements.

The type of radioactivity alpha or beta rays is given in small circles, the half-life is written under the element, and the chemical properties are indicated by the roman numerals which give the group in the periodic table (page 665).

Fajans and Soddy placed these radioelements in the periodic table as shown in **Fig. 151** and pointed out in 1913 that the emission of an alpha particle causes a radioactive element to shift its position in the periodic table two places in the direction of decreasing atomic weights, and the emission of a beta particle causes it to shift one place in the periodic table in the opposite direction.

When an alpha particle with its mass of four and its two positive charges is emitted, the new nucleus weighs four units less and has two

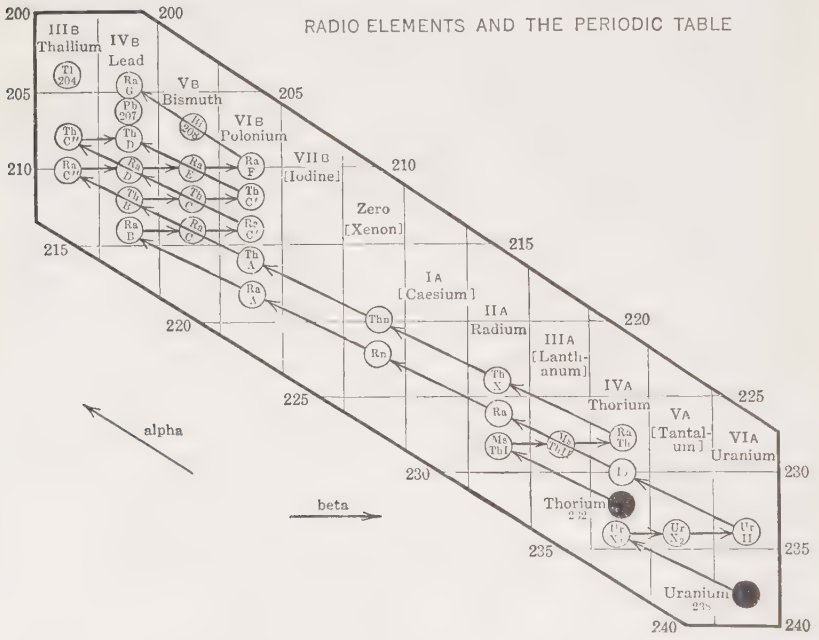


FIG. 151. The positions of the heavy radioactive elements in the periodic table.

positive charges less. The charge on the nucleus is the atomic number, and, hence, the atomic number decreases by two. When a beta particle with its negative charge is emitted, there is no appreciable loss of mass, but the positive charges on the nucleus are increased by one; that is, the atomic number increases by one.

A striking feature of this table is the fact that the decay series of uranium and thorium lead to the occurrence of several individual members of a group which occupy the same position in the periodic table and have the same chemical properties but have different atomic weights. These different substances having the same chemical properties but different atomic weights are called *isotopes*.

Mass Spectrometer. The positive ions in an electric discharge are repelled by the anode and move rapidly toward the cathode. If a tube with a perforated cathode is used, they will pass through the perforations into the space behind the cathode where their properties may be studied. These rays were called *positive rays* by Sir J. J. Thomson, who used an ingenious method for the determination of the individual masses of the positively charged particles by sifting them out onto a photographic plate. The mass spectrometer for separating ions of different mass has been constantly improved until now the atomic masses of isotopes can be determined with much greater accuracy than the atomic weights can be determined by chemical means.

The principle of the mass spectrograph is illustrated in **Fig. 152.** A beam of positive ions is produced by bombardment of gaseous ions with electrons from a heated filament at a definite potential and thrown out through the slits s_1 and s_2. The particles then pass through the electrostatic field X between E_1 and E_2, at right angles to which there is also an electromagnetic field H. Only those ions which have a velocity equal to X/H will pass through slit s_3; the others will all curve around so as to miss the exit slit. All ions that do get through have the same velocity, and they are curved around by a powerful magnetic field through an arc of 180° so as to hit the photographic plate P.

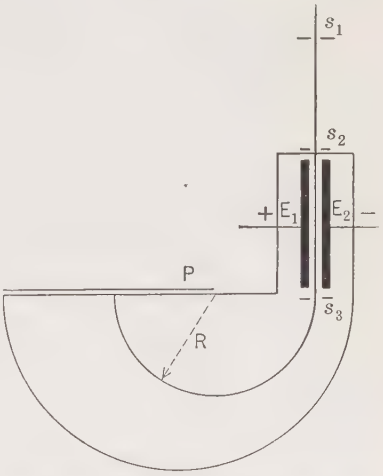


FIG. 152. Principle of the mass spectrograph.

The radius of curvature of the ion beam represented by R is given by the relation:

$$R = \frac{mv}{eH} \tag{11}$$

Since the charge on the ion, the magnetic field, and the velocity are all constant, the radius or the position on the photographic plate is directly proportional to the mass. The plate is calibrated with ions of known mass.

Care is necessary in the interpretation of results because the particles may have two or more charges, and there may be ionized fragments of

molecules, such as CH^+, CH_2^+, and CH_3^+; or hydrides may be formed with impurities of hydrogen.

Often it is important to know not only what isotopes are present but also their relative abundance. The blackening on a photographic plate

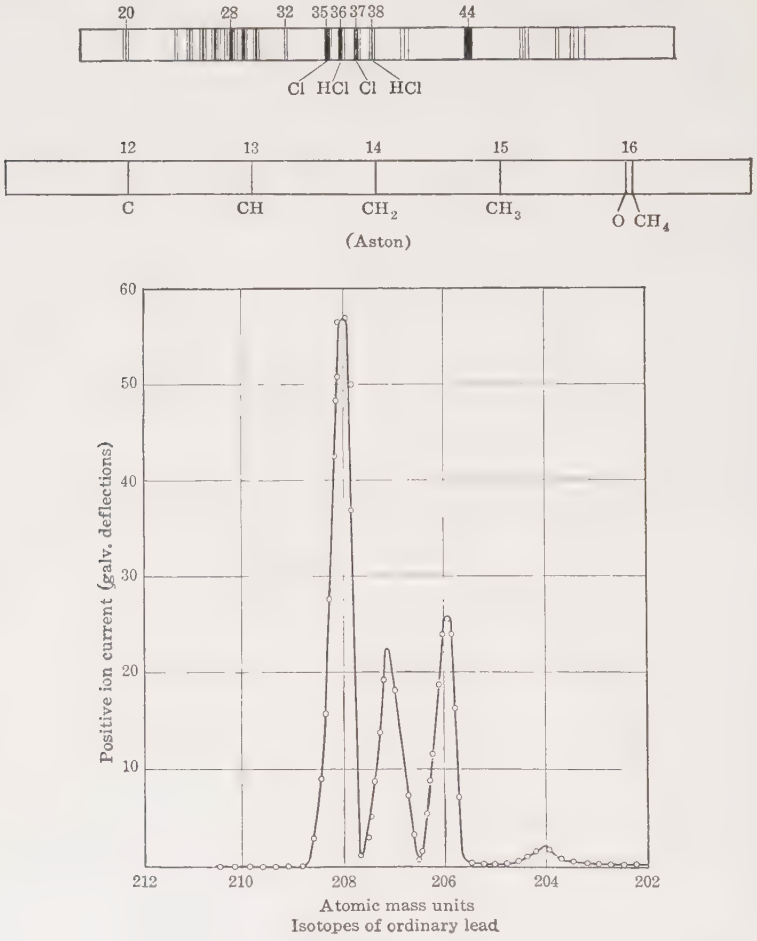


FIG. 153. Isotopes of elements as determined with the mass spectrometer.

is an approximate measure of the ions hitting the plate at a given position, but better results can be obtained with an electrical method in which all the ions entering a slit are caught in a chamber from which the charges leak off through an electric circuit. The feeble currents are amplified with electron tubes and read with a galvanometer. Instead of moving the slit along to intercept ion beams having different ratios

of m/e, it is simpler to change the accelerating voltage. The galvanometer reading at a setting of a given isotope is a measure of the number of ions and the ratio of peaks in the ionization current is a direct measure of the ratio of the abundance of the isotopes.

In **Fig. 153** the first two mass spectrograms are taken from measurements of Aston on the isotopes of chlorine and the fragments of methane produced by the action of electrons on methane.

The isotopes of chlorine 35 and 37 and the corresponding hydrides 36 and 38 are clearly shown. In the second spectrogram the slight difference in mass between oxygen and methane is evident.

In the lowermost figure, taken from the work of Nier,* the relative abundance of the different isotopes of lead is given by the heights of the peaks obtained when the galvanometer deflections are plotted against the mass of the isotopes.

The isotopes of cadmium are shown in **Fig. 154** as obtained by Professor A. J. Dempster † of the University of Chicago using a sensitive mass spectrograph. The differences in the two spectra are discussed later.

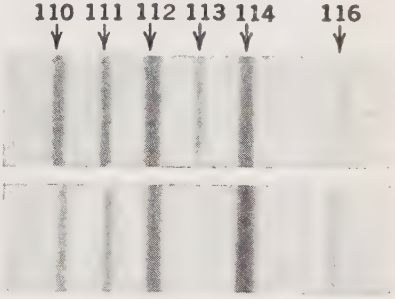


FIG. 154. Isotopes of cadmium.

The mass spectrometer developed by Nier is convenient for determining isotope ratios in tracer experiments. Metal chambers and slit systems are attached with special seals to a long tube of glass, with a curve in the middle which passes between the V-shaped poles of an electromagnet. Less than a milligram of material is needed for an analysis, and, when the spectrometer is operating properly, analysis may be made rapidly with an error of less than 0.1 per cent in the abundance ratio.

Extensive use has been made of the mass spectrometer as an analytical tool for following the separation of isotopes and for studying petroleum reactions. Some of the fragments of organic vapors produced by thermal decomposition can be found with the mass spectrometer, particularly if the ionization voltage for producing the ions is below the ionization potential of the undecomposed molecules.

Occurrence of Isotopes. The development of the mass spectrograph as a precision instrument has led to the discovery of a large number of isotopes. The reference standard for chemical atomic weights is ordi-

* Nier, *J. Am. Chem. Soc.*, **60**, 1572 (1938).

† Dempster, *Phys. Rev.*, **71**, 829 (1947).

nary oxygen taken as 16, which is really a mixture of isotopes with the distribution $O^{16} = 498.8$: $O^{17} = 0.2$: $O^{18} = 1$. The reference standard for the mass numbers, obtained with the mass spectrometer, is the lightest isotope of oxygen O^{16}. It is a more definite standard than the ordinary oxygen in which the isotope ratios may change slightly, and it can be determined with greater accuracy than the chemical atomic weights, but in all chemical and physical-chemical calculations the chemical atomic weights are used.

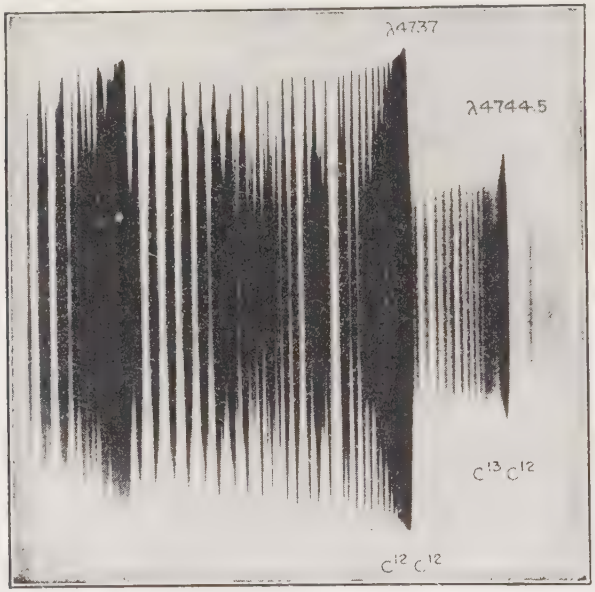


Fig. 155. Band spectra of carbon showing different spectra due to isotopes of carbon.

Since the standard of atomic *mass* O^{16} is lighter than the mixture of oxygen isotopes, 1.000000 unit on the chemical or weight scale is equal to 1.000272 on the physical or mass scale.

It has been known since 1913 that the atomic weight of lead can vary, depending on the source of the material. Lead obtained, for example, from a radioactive ore rich in uranium has a higher atomic weight than lead which is derived in part from the radio disintegration of thorium because the isotopes of lead from uranium are heavier. This situation may be understood by reference to Fig. 151. Moreover, it has been pointed out by Urey that in the lighter elements the atomic-weight measurements have about reached the limit of useful accuracy and that, if further accuracy is obtained, it will be necessary to take account of the concentration of isotopes which inevitably accompanies the chemical and physical operations of purification and analysis.

In Table III on page 640 are listed a few elements with their exact atomic masses obtained on the basis of mass spectrometer data together with the relative abundance of the different isotopes.

The presence of oxygen isotopes having masses of 16, 17, and 18 was discovered by a study of bands in the absorption spectrum of the sun as its light passed through the atmosphere surrounding the earth. The heavier isotope of hydrogen, deuterium, was discovered by the appearance of a new neighboring line in the emission spectrum after continued fractional distillation of hydrogen. The discovery of the heavier isotope of carbon, C^{13}, is shown in **Fig. 155.** This spectrogram, reproduced with the permission of the University of Chicago Press, was obtained by King and Birge * in carbon vapor at high temperatures. The band of lesser intensity due to the molecule $C^{12} - C^{13}$ is plainly evident at the right.

Concentration of Isotopes. The ratio of isotopes may be altered by fractional diffusion or evaporation, or by centrifuging, or, in fact, by any physical or chemical method which makes use of the difference in weights. It will be remembered that the relative velocities of molecules are inversely proportional to the square roots of the molecular weights. Effective concentration of small quantities of isotopes has been accomplished in the lighter elements with a battery of mercury diffusion pumps operating in series.†

One of the simplest methods for concentrating isotopes combines thermal diffusion and convection. When a vertical central wire or tube is maintained at a temperature 200 or 300° above the walls of a larger containing tube and allowed to stand, the heavier constituents of an enclosed gas concentrate at the bottom of the tube.‡ Bromine and air in a glass tube can be seen to separate within a few minutes. In such a tube 60 ft high filled with methane the carbon at the bottom of the tube becomes enriched with C^{13} in a few weeks from 1 per cent to several per cent, and by flowing a fresh supply of methane through slowly at the top it is possible to draw off at the bottom over 100 ml per day of the methane enriched with C^{13}.§

Isotopes may be separated also by chemical means, although isotopes were originally thought to have identical chemical properties. The natural vibration frequency of atoms in a molecule depends to a slight extent on the mass of the atoms involved, and this vibration frequency

* King and Birge, *Astrophys. J.*, **72,** 24 (1930).

† Hertz, *Z. Physik*, **79,** 108 (1932).

‡ Clusius and Dickel, *Naturwiss.*, **26,** 546 (1938); **27,** 149 (1938); Brewer and Bramley, *Phys. Rev.*, **55,** 590 (1939).

§ Taylor and Glockler, *J. Chem. Phys.*, **7,** 850 (1939); **8,** 843 (1940).

affects the "zero point energy," or the energy requirement at the very bottom of the Morse curve shown in Fig. 141 on page 588. In other words, there is a very slight difference in the activation energies for chemical reactions involving the isotopes. In competing reactions, then, the heavier isotope should react somewhat more slowly. The difference is sufficient for complete separation in the case of hydrogen where the masses are 1 and 2, but there is a chance also for a slight concentration of isotopes in the other light elements. This slight difference in reactivity shows up also in the position of chemical equilibrium.* For example, the equilibrium constant for the reaction,

$$N^{15}H_3\ (g) + N^{14}H_4^+\ (aq) = N^{14}H_3\ (g) + N^{15}H_4^+\ (aq)$$

is not unity; calculations show that it is 1.033. Thode and Urey † carried out experimental concentration of N^{15} using this reaction in an effective column passing the ammonia gas up against a solution of ammonium nitrate flowing down. Concentration of N^{15} up to 72 per cent was obtained, and the experimentally determined value of K was 1.023. It is now possible to purchase ‡ ammonium nitrate containing 30 per cent of the ammonium nitrogen as heavy nitrogen N^{15}. Heavy carbon C^{13} has been prepared by a similar method, using HCN gas and NaCN solution.

The separation of isotopes has been considered as a very difficult laboratory operation, but during the last few years uranium 235 has been separated from uranium 238 on a large scale by two different methods. In one method the principle of the mass spectrometer was used. A volatile compound of uranium was ionized and shot out as streams of charged particles which were then separated by the differences in deflection in the field of a very large electromagnet.

In the second method the uranium compound was allowed to diffuse through small holes in special barrier plates, the uranium 235 compound diffusing at a slightly faster rate than the uranium 238 compound. Continuous operations with special machinery, on a very large scale, resulted in the accumulation of uranium 235.

Stable isotopes of many of the elements have been separated by the electromagnetic method and are available for research throughout the world.§

* Urey and Greiff, *J. Am. Chem. Soc.*, **57**, 321 (1935).

† Thode and Urey, *J. Chem. Phys.*, **7**, 34 (1939).

‡ Eastman Kodak Co., Rochester, N. Y.

§ They can be rented at a nominal price from the U. S. Atomic Energy Commission at Oak Ridge, Tenn.

It is likely that all the slight differences in *chemical* behavior of isotopes, which makes their separation possible, have not yet been explored. The kinetic method, utilizing competing reactions which are not in equilibrium, should be investigated.

A simple and effective means of separating the isotopes of hydrogen in these competitive reactions was found in the electrolysis of water.* Hydrogen contains 1 part of H^2 in about 5000 parts of H^1, and, if most of the water in a given sample is electrolyzed away, the residue of water containing the last hydrogen to come off in the electrolysis is much richer in H^2.†

The properties of this heavy isotope of hydrogen are so different from ordinary hydrogen that a special name was assigned to it—*deuterium*, the symbol for which is D. The process on a large scale now provides practically pure D_2O at about 50 cents per gram.

The properties of water and heavy water are compared in Table I.

TABLE I

PROPERTIES OF D_2O AND H_2O

	Specific Gravity 20°	Freezing Point	Boiling Point	Heat Vaporization per Mole	Surface Tension 20°	Viscosity 20° $\times 10^3$	Dielectric Constant	Refractive Index n_D^{20}	Solubility NaCl grams per 1000 g
D_2O	1.1059	3.82°	101.42°	9960	67.8	12.6	80.5	1.32844	305
H_2O	0.9982	0.00	100.00	9700	72.75	10.09	82.0	1.33300	359

The Neutron. In 1932 the *neutron* was discovered by Chadwick. Previous investigators had bombarded light elements with alpha particles and obtained ionization effects at great distances. The nature of these penetrating radiations was in doubt. Chadwick bombarded beryllium with alpha particles and showed by the great penetration, by the failure to produce cloud tracks, and by the failure to be deflected in a magnetic field that the effects were produced by an uncharged particle having the mass of the hydrogen atom. Moreover, these particles were absorbed by paraffin and other hydrogen-containing materials, whereas they would penetrate many substances of much greater density. This specific absorption indicated a new unit of matter with new properties. This unit, called the neutron, had been predicted by Rutherford and by Harkins.

* Washburn and Urey, *Proc. Natl. Acad. Sci.*, **18**, 496 (1932).

† Lewis, *J. Am. Chem. Soc.*, **55**, 1297 (1933).

Neutrons can be detected by the ionizing particles which are produced when they are absorbed by the nuclei of certain atoms, such as boron. An ionization chamber can be filled with a volatile boron compound, or a solid boron compound can be used as a target in a Geiger–Müller counter. The amount of ionization measured is directly proportional to the number of neutrons which are absorbed by the boron target.

The neutron has approximately the mass of a hydrogen atom or proton, but it has no charge. Owing to the absence of an electric charge, it is much more penetrating than alpha particles or beta particles. The neutrons suffer collision with atoms and acquire velocities which can be calculated on the basis of the Maxwell–Boltzmann theory, with a distribution which depends on temperature in the same way that the distribution of molecular velocities depends on temperature. When neutrons are emitted in fission (page 656), they may have very great velocities, corresponding to millions of electron volts. Their velocities are quickly reduced to those prevailing at room temperature by collisions with surrounding atoms, the light atoms with masses not greatly different from that of the neutrons being the most effective.

Neutrons are absorbed by many different elements and isotopes. The efficiency of absorption is highly specific, as illustrated by the fact that neutrons will pass through deuterium compounds easily, but they are readily absorbed by hydrogen compounds.

Nuclear Units. Rutherford found that, when alpha particles were passed through a thin sheet of metal, most of them continued their straight paths, but occasionally an alpha particle would suffer a large deflection. Remembering that these alpha particles, with a mass four times that of a hydrogen atom, are traveling with one-tenth the velocity of light, he calculated that the large deflections cannot be explained on the basis of uniform distribution of matter but must be due to a collision with material of greater density than anything which had heretofore been imagined. He came to the conclusion that the mass of the atom must be centered in a nucleus occupying a very small volume. Another line of evidence for atomic nuclei came from the hypothesis of Bohr in 1913. It was shown on page 570 that the lines of the hydrogen spectrum can be accurately predicted on the assumption of an electron moving around a central charged nucleus in elliptical orbits. The initial success of this model was so great in interpreting the spectral lines in many elements that the idea of an atomic nucleus of great density became well established.

Our knowledge of the composition of the nucleus and the fundamental units of which matter is composed was greatly advanced in 1932, when, as already explained, the neutron was discovered. In the same year, the *positron* was discovered by Anderson, during an examination

in a cloud chamber of particles emitted during the bombardment of a gas by cosmic rays. A powerful magnetic field of known strength was placed across the chamber, and cloud tracks were obtained with such a large curvature that the particle producing the track could have a mass only of 0.000549 on the atomic weight scale, that is, the mass of an electron. But the curvature was in the wrong direction. In previous experiments, there was no way of telling in which of the two directions along the cloud track the particle was traveling. In this particular experiment the particle passed through a thin lead sheet, and a photograph was taken at right angles to the sheet. It showed the curvature of the path on one side to be greater than that on the other, and, hence, the particle was traveling through the lead in the direction pointing to the greater deflection (lower velocity). The observed curvature in the magnetic field could be explained only on the assumption that the particle was charged *positively*. There has been abundant proof of the occurrence of these positively charged "electrons."

Also in 1932 Urey discovered the heavy isotope of hydrogen H^2 or *deuterium*. The nucleus of this atom has a mass of 2 and one positive charge and is called the *deuteron*. The *meson* has a mass about 200 times that of the electron. It is produced from nuclei by cosmic rays or by particles of extremely high energy.

Our building blocks of all matter then are given in Table II. Although electrons and positrons are given off when certain atomic nuclei disintegrate, they do not necessarily exist in the nuclei as separate entities.

TABLE II

PRIMARY UNITS

Unit	Symbol	Mass [1]	Charge
Proton [2]	p	1.007582	+
Electron	e, β^-	0.000549	−
Neutron	n	1.00893	0
Positron	e^+, β^+	0.000549	+
Deuteron	d	2.014176	+
Alpha particle	α	4.002763	2+
Meson		$\backsim$0.01	

[1] On the physical scale.

[2] The mass of the hydrogen atom is 1.007582 + 0.000549 = 1.00813.

The nuclei of the atoms are composed of protons and neutrons. The number of protons in the nucleus is the atomic number, which determines the chemical properties. The sum of the protons and the neutrons gives approximately the mass of the nucleus. The mass of the atom is

slightly greater than that of the nucleus on account of the presence of the electrons which surround the nucleus—0.000549 on the atomic weight scale for each electron. The number of electrons is equal to the atomic number.

A given element may be composed of several different isotopes, each having the same number of protons and, hence, the same nuclear charge and atomic number, but different numbers of neutrons and, hence, differing atomic masses. The atomic weight of the element is a weighted average of the masses of all the isotopes of which the element is composed.

These fundamental relations are illustrated in Table III. Not all the

TABLE III

Composition of Some Atomic Nuclei

Element	Symbol	Atomic Number (Number of Protons)	Number of Protons + Number of Neutrons	Atomic Mass of Isotope	Abundance, per cent	Atomic Weight of Element, Chemical Scale
Hydrogen	$_1H^1$	1	1 + 0 = 1	1.0081	99.98	1.0080
Deuterium	$_1H^2$	1	1 + 1 = 2	2.0147	0.02	
Tritium	$_1H^3$	1	1 + 2 = 3	3.0170	unstable	
Lithium	$_3Li^6$	3	3 + 3 = 6	6.0170	7.5	6.940
	$_3Li^7$	3	3 + 4 = 7	7.0182	92.5	
Carbon	$_6C^{12}$	6	6 + 6 = 12	12.0038	98.9	12.010
	$_6C^{13}$	6	6 + 7 = 13	13.0075	1.1	
	$_6C^{14}$	6	6 + 8 = 14	14.0077	unstable	
Nitrogen	$_7N^{13}$	7	7 + 6 = 13	13.0099	unstable	
	$_7N^{14}$	7	7 + 7 = 14	14.0075	99.62	14.008
	$_7N^{15}$	7	7 + 8 = 15	15.0049	0.38	
Oxygen	$_8O^{16}$	8	8 + 8 = 16	16.0000	99.76	16.000
	$_8O^{17}$	8	8 + 9 = 17	17.0045	0.04	
	$_8O^{18}$	8	8 + 10 = 18	18.0049	0.20	
Chlorine	$_{17}Cl^{35}$	17	17 + 18 = 35	34.9787	75.4	35.457
	$_{17}Cl^{37}$	17	17 + 20 = 37	36.9775	24.6	
Copper	$_{29}Cu^{63}$	29	29 + 34 = 63	63	70.13	63.54
	$_{29}Cu^{65}$	29	29 + 36 = 65	65	29.87	
Lead	$_{82}Pb^{206}$	82	82 + 124 = 206	206	23.6	207.21
	$_{82}Pb^{207}$	82	82 + 125 = 207	207	22.6	
	$_{82}Pb^{208}$	82	82 + 126 = 208	208	52.3	
Uranium	$_{92}U^{234}$	92	92 + 142 = 234	234	0.005	238.07
	$_{92}U^{235}$	92	92 + 143 = 235	235	0.72	
	$_{92}U^{238}$	92	92 + 146 = 238	238	99.27	

isotopes are shown in this table. For example, in addition to the two stable isotopes 35 and 37, chlorine has four unstable isotopes, which can be produced in the laboratory, each with 17 protons and the following number of neutrons: 16, 17, 19, 21. Most of the known isotopes are recorded in Table VI on page 647.

Transmutation. It was known that the heaviest metals disintegrate spontaneously, and attempts were made to disintegrate other elements by artificial means. Alpha particles with their enormous kinetic energy were used successfully as missiles by Rutherford and Chadwick in 1921 to disintegrate nitrogen atoms. The alpha particles have a definite range in nitrogen of about 7 cm, but some flashes of light, apparently due to the impact of fast-moving particles, could be detected on a sensitive screen at much greater distances. Deflections in a magnetic field indicated that the particles which caused these scintillations were protons. It might be expected that, if an alpha particle hits a hydrogen atom squarely, the hydrogen atom with a mass one fourth as great could travel considerably farther—up to 28 cm. As a matter of fact, in pure nitrogen, flashes were detected up to a distance of 40 cm. Such a great range was explained on the hypothesis that the nucleus of the nitrogen atom is actually altered by the collision with the alpha particle, and intra-atomic energy is released which drives the proton out with great additional force. Several other light elements such as boron and fluorine were disintegrated in the same way.

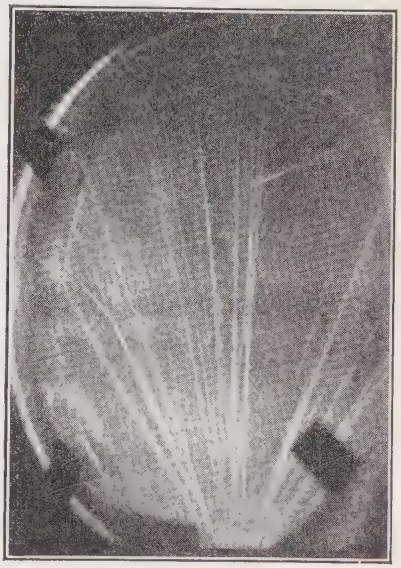


Fig. 156. Disintegration of nitrogen nucleus by alpha particle as shown by cloud tracks.

An actual disintegration of a nitrogen nucleus by bombardment with an alpha particle is shown in **Fig. 156** taken from an early photograph by Professor W. D. Harkins of the University of Chicago.* This photograph is one of some 34,000 photographs of the cloud tracks of alpha particles. Most of the tracks are straight lines, as indicated schematically in Fig. 149 on page 625, but the second track from the left just below the middle of Fig. 156 shows a sharp deflection to the

* Harkins and Shadduck, *Proc. Natl. Acad. Sci.*, **12**, 709 (1926).

left and a very faint horizontal line (visible in the original). In this rare collision the alpha particle made a direct hit on the nucleus of the nitrogen atom, and the new nucleus is unstable, with the result that a proton is expelled horizontally to the right, and the remaining stable nucleus, probably O^{17} goes off toward the left. A measurement of the angles of branched tracks of this type permit calculations of the energies released.

The study of the atomic nucleus received a great impetus when projectiles other than alpha particles were used for bombardment. Protons or deuterons, traveling at enormous velocities under potentials of a million volts and more, are effective in disintegrating nuclei. Several different types of apparatus are used for the acceleration. In the cyclotron, developed by Lawrence at the University of California, the ions are subjected to a moderately high voltage and guided around a spiral path by a powerful magnetic field. The voltage is altered at just the right frequency so that the ions (protons, deuterons, or helium nuclei) are accelerated each time they make one half-circle, and the applied voltage is thus cumulative. As the projectiles attain higher and higher voltages they move in circles of increasing radius, and, when they reach the outer edge of the apparatus, they are deflected by an electric field against a target of the material which is to be bombarded.

In the electrostatic generator, a rapidly moving belt carries electricity from charged points to a cylindrical or spherical electrode until a very high steady voltage is reached. The difficulties of insulation have been solved by placing the whole apparatus in a large steel tank containing gas at several atmospheres pressure to increase the resistance against sparking.* A series of metal hoops is arranged to give a gradual change of potential along an evacuated tube, within which the ions are accelerated.

The electrostatic generator gives energies up to about 6 million volts, and it is especially useful for carrying out nuclear transformations at definite and controlled voltages.

In **Fig. 157** the intensity of gamma-ray radiation is plotted against voltage when the nuclei of fluorine atoms are bombarded with protons.† Calcium is not transmuted by protons at these voltages, and so calcium fluoride is used as the target. The peaks in the voltage-excitation curve correspond to stable energy levels in the nucleus. Their resemblance to the peaks in the ionization potential curves of atoms shown in Fig. 134 on page 577 is evident. Energy changes in the extranuclear electrons involve a few volts, whereas changes in the nucleus of an atom usually require voltages of the order of a million electron volts or more.

* Herb, Parkinson, and Kerst, *Phys. Rev.*, **51**, 76 (1937).

† Bernet, Herb, and Parkinson, *Phys. Rev.*, **54**, 398 (1938).

Several cyclotrons have been built with energies which give to the bombarding protons, deuterons, or helium ions energies up to 20 million electron volts. Recent developments have resulted in the successful operation of a cyclotron 184 in. in diameter, which produces bombarding particles with energies up to 200-million-electron-volt deuterons or 400-million-electron-volt alpha particles from helium.

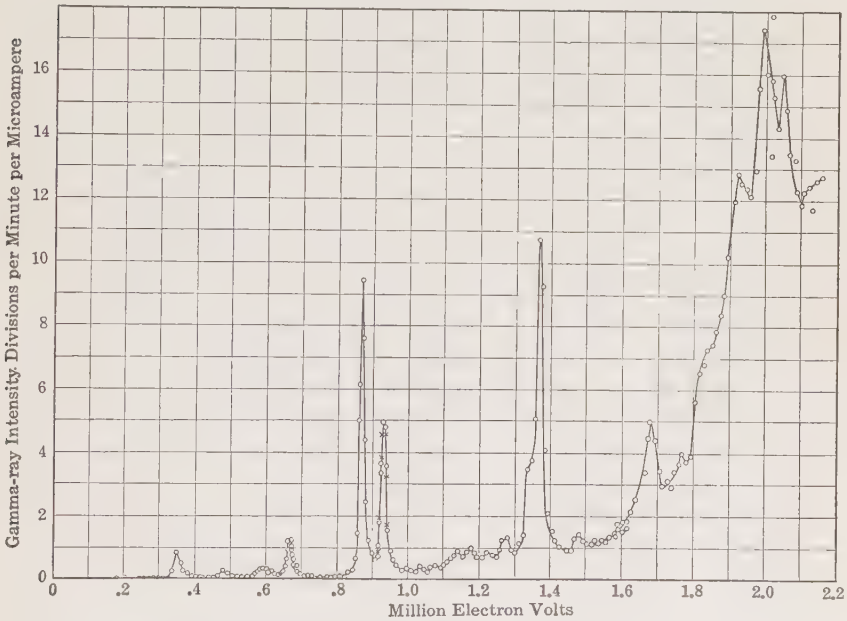


Fig. 157. Energy levels in the nucleus of fluorine.

The transmutation of elements can be brought about as just explained by giving enormous velocity to charged particles, protons, deuterons, and helium ions so that they can penetrate the surrounding layers of electrons and reach the nucleus of the atom.

The nucleus can be reached, however, much more easily by neutrons, because they do not have an electric charge. The shells of electrons, then, do not constitute a strong barrier against these neutral neutrons. Accordingly the neutrons attach quite readily to atomic nuclei of many isotopes of the elements and bring about a variety of transmutations.

Fermi, in Italy in 1935, exposed most of the elements in the periodic table to neutrons and obtained a large number of new isotopes.

Neutrons for these transmutations can be produced by mixing radium compounds with beryllium compounds or by bombarding beryllium or lithium targets with a beam of fast deuterons from a cyclotron or an

electrostatic generator. These sources of neutrons give only small amounts of new isotopes, but, with the vast new sources of neutrons from nuclear chain-reacting piles described on page 657, the way has been opened now for the production of much larger quantities of transmuted elements and isotopes.

Gamma rays of very high energies liberated from certain nuclear reactions are able to bring about nuclear reactions similar to photochemical reactions. Cosmic rays coming from interstellar space are also able to effect nuclear transmutations.

The concentration of radioactive elements may be facilitated if the nuclear reaction produces also a chemical reaction which permits a separation from the original material, as was pointed out first by Szillard and Chalmers. For example, when a bottle of ethyl bromide is exposed to neutrons, the bromine atoms which are rendered radioactive are broken away from their organic linkages and can be extracted with water containing a little alkali. In this way the ratio of radioactive to normal bromide is greatly increased in the aqueous solution.

Nuclear Reactions. In 1932, Irene Curie, daughter of the discoverers of radium, with her husband, F. Joliot, discovered that ordinary light elements can be made radioactive. They bombarded boron and aluminum and other light elements with alpha particles and obtained an emission of positrons which continued after the excitation by the alpha particles had ceased.

With magnesium the reaction is

$$_{12}\mathrm{Mg}^{24} + {}_{2}\mathrm{He}^{4} \rightarrow {}_{14}\mathrm{Si}^{27} + {}_{0}n^{1}$$

The silicon produced from the magnesium is radioactive with a half-life of 4 seconds and gives off positrons, leaving a stable isotope of aluminum according to the reaction:

$$_{14}\mathrm{Si}^{27} \rightarrow {}_{13}\mathrm{Al}^{27} + \beta^{+}$$

In writing nuclear reactions it is necessary to balance them with respect to mass and charge. In other words, the sum of the superscripts (mass numbers) on the left must be equal to the sum of the superscripts on the right; and the sum of the subscripts (atomic numbers) on both sides must be equal also.

Most artificial radioelements emit electrons (β^{-}) or positrons (β^{+}), but other types of decay also occur. In some cases a given isotope may undergo disintegration by one of two or even three different processes.

Some isotopes involve the nuclear process known as *K-electron capture*, in which an external electron from the shell nearest the nucleus,

the K shell, enters the nucleus, causing the atomic number to decrease by one unit. The filling of the vacancy in the K shell by other electrons causes the emission of X rays from the atom.

Frequently, the emission of a particle, capture of an electron, or other nuclear process leaves a nucleus in an unstable condition, and it acquires a state of greater stability by the immediate emission of one or more gamma rays. Occasionally, however, such a higher-energy state may be metastable, which leads to the existence of *nuclear isomers* having the same atomic weight as well as the same atomic number. For example, the bromine isotope $_{35}Br^{80}$ characterized by a half-life of 4.4 hours emits gamma radiation without loss of either mass or charge, the *isomeric transition* resulting in the isotope having a half-life of 18 minutes.

Sometimes associated with gamma radiation are so-called *conversion electrons*. The nucleus interacts with an outer electron and expels it with high speed instead of emitting a gamma ray. Such a process leaves the atom in an excited state of high-energy content, which often results in chemical reactivity. In such cases as $_{35}Br^{80}$, where the product is radioactive, its chemical nature may be traced by its radioactivity.

The processes by which radioelements are produced fall into a few general types. The reaction,

$$_{12}Mg^{24} + {}_{2}\alpha^{4} \rightarrow {}_{14}Si^{27} + {}_{0}n^{1}$$

is an example of the type reaction:

$$_{Z}X^{M} + {}_{2}\alpha^{4} \rightarrow {}_{Z+2}Y^{M+3} + {}_{0}n^{1}$$

A simplified notation for the same reaction is

$$Mg^{24}(\alpha, n)Si^{27}$$

where the first symbol in the parentheses is the bombarding particle, and the second is the emitted particle. A few examples of nuclear reactions are given in Table IV, and a summary of the principal types is given in Table V.

TABLE IV

Typical Nuclear Reactions

General Reactions	Example	Notation
$_{Z}X^{M} + {}_{0}n^{1} \rightarrow {}_{Z}Y^{M+1} + {}_{0}\gamma^{0}$	$_{25}Mn^{55} + {}_{0}n^{1} \rightarrow {}_{25}Mn^{56} + {}_{0}\gamma^{0}$	$Mn^{55}(n, \gamma)Mn^{56}$
$_{Z}X^{M} + {}_{1}p^{1} \rightarrow {}_{Z+1}Y^{M} + {}_{0}n^{1}$	$_{3}Li^{7} + {}_{1}p^{1} \rightarrow {}_{4}Be^{7} + {}_{0}n^{1}$	$Li^{7}(p, n)Be^{7}$
$_{Z}X^{M} + {}_{2}\alpha^{4} \rightarrow {}_{Z+1}Y^{M+3} + {}_{1}p^{1}$	$_{20}Ca^{43} + {}_{2}\alpha^{4} \rightarrow {}_{21}Sc^{46} + {}_{1}p^{1}$	$Ca^{43}(\alpha, p)Sc^{46}$
$_{Z}X^{M} + {}_{1}d^{2} \rightarrow {}_{Z+1}Y^{M} + 2{}_{0}n^{1}$	$_{52}Te^{130} + {}_{1}d^{2} \rightarrow {}_{53}I^{130} + 2{}_{0}n^{1}$	$Te^{130}(d, 2n)I^{130}$
$_{Z}X^{M} + {}_{0}n^{1} \rightarrow {}_{Z-2}Y^{M-3} + {}_{2}\alpha^{4}$	$_{27}Co^{59} + {}_{0}n^{1} \rightarrow {}_{25}Mn^{56} + {}_{2}\alpha^{4}$	$Co^{59}(n, \alpha)Mn^{56}$

TABLE V

PRINCIPAL NUCLEAR REACTIONS

Neutron Reactions	Deuteron Reactions	Proton Reactions	Alpha Reactions	Photonuclear Reactions
n, γ	d, p	p, n	α, n	γ, n
$n, 2n$	d, n	p, γ	α, p	
n, p	d, α	p, α		
n, α	$d, 2n$			

A good demonstration of the nuclear reaction produced by neutrons was shown in Fig. 154 obtained by Professor A. J. Dempster, of the University of Chicago. The upper mass spectrogram of ordinary cadmium shows isotopes 111, 112, 113, and 114. The lower spectrogram was obtained from surface scrapings of cadmium that had been exposed to neutron irradiation for a long time in an atomic pile, page 657. The neutron reaction is

$$_{48}\mathrm{Cd}^{113} + n = {}_{48}\mathrm{Cd}^{114}$$

The concentration of Cd^{113} in the mixture of cadmium isotopes has been reduced from 12.3 to 1.6 per cent, and that of Cd^{114} has been increased from 28 to 39 per cent. Within the accuracy of the measurements the gain of cadmium 114 is practically equal to the loss of cadmium 113, whereas there has been very little change in the concentrations of the other isotopes. Cadmium 113 has a very great absorption for neutrons, so great, in fact, that cadmium is used in various experiments where it is desired to screen out neutrons having low velocities.

In Table VI are listed most of the stable and unstable isotopes.* The symbols of the elements and their atomic numbers are given in the first two columns. The next column gives the mass numbers of the isotopes with the approximate per cent of abundance of the isotope in the naturally occurring element. The last column gives the mass numbers of the unstable radioactive isotopes followed in parentheses by the type of decay α, β^-, β^+ or γ and by K for K-electron capture, IT for isomeric transition, and C for internal conversion electron. The half-life of the isotope is given in seconds s, minutes m, days d, or years y.

The atomic number is the number of protons in the nucleus and the mass number is the sum of the protons and neutrons in the nucleus. Accordingly, the number of neutrons in any isotope can be obtained by subtracting the number of protons from the mass number.

* A complete table has been prepared by Seaborg, *Rev. Mod. Phys.*, **16**, 1 (1944). A chart prepared by Segre can be purchased from the Addison Wesley Press, Inc., Cambridge, Mass.

A summary of nuclear data for 1947 has been compiled, *Nucleonics*, **2** (5), 82–186 (1948).

TABLE VI

STABLE AND UNSTABLE ISOTOPES OF THE ELEMENTS

Element	At. No.	Stable Isotopes (Per Cent Abundance)	Radioactive Isotopes (Radiation; Half-life [1])
H	1	1 (99.98); 2 (0.02)	3 (β^-, $-31y$)
He	2	3 ($\backsim 10^{-5}$); 4 (100)	6 (β^-, $-0.8s$)
Li	3	6 (7.5); 7 (92.5)	8 (β^-, $0.88s$)
Be	4	9 (100)	7 (γ, $43d$); 10 (β^-, $>10^6y$)
B	5	10 (18.4); 11 (81.6)	12 (β^-, $0.02s$)
C	6	12 (98.9); 13 (1.1)	10 (β^+, $8.8s$); 11 (β^+, $20.5m$); 14 (β^-, $4700y$)
N	7	14 (99.62); 15 (0.38)	13 ($\beta^+\gamma$, $9.93m$); 16 ($\beta\gamma$, $8s$)
O	8	16 (99.76); 17 (0.04); 18 (0.20)	15 (β^+, $126s$); 19 ($\beta^-\gamma$, $31s$)
F	9	19 (100)	17 (β^+, $70s$); 18 (β^+, $112m$); 20 ($\beta^-\gamma$, $12s$)
Ne	10	20 (90.00); 21 (0.27); 22 (9.73)	19 (β^+, $20.3s$); 23 (β^-, $40s$)
Na	11	23 (100)	21 (?, $23s$); 22 ($\beta^+\gamma$, $3.0y$); 24 ($\beta^-\gamma$, $14.8h$); 25 ($\beta^-\gamma$, $62s$)
Mg	12	24 (77.4); 25 (11.5); 26 (11.1)	23 (β^+, $11.6s$); 27 ($\beta^-\gamma$, $10.2m$)
Al	13	27 (100)	26 (β^+, $7.0s$); 28 ($\beta^-\gamma$, $2.4m$); 29 (β^-, $6.7m$)
Si	14	28 (89.6); 29 (6.2); 30 (4.2)	27 (β^+, $4.9s$); 31 (β^-, $170m$)
P	15	31 (100)	29 (β^+, $4.6s$); 30 (β^+, $2.55m$); 32 (β^-, $14.30d$); 34 ($\beta^-\gamma$, $12.4s$)
S	16	32 (95.1); 33 (0.74); 34 (4.2)	31 (β^+, $3.2s$); 35 (β^-, $87.1d$); 37 ($\beta^-\gamma$, $5m$)
Cl	17	35 (75.4); 37 (24.6)	33 (β^+, $2.4s$); 34 (β^+, $33m$); 36 ($\beta^+K\beta^-$, $>10^5y$); 38 ($\beta^-\gamma$, $37m$)
A	18	36 (0.307); 38 (0.061); 40 (99.6)	35 (β^+, $1.88s$); 37 (K, $34d$); 41 ($\beta^-\gamma$, $110m$)
K	19	39 (93.38); 41 (6.61)	38 (β^+,$7.7m$); 40 ($\beta^-\gamma$, K, 4×10^8y); 42 ($\beta^-\gamma$, $12.4h$); 43 (β^-, $18m$)
Ca	20	40 (96.96); 42 (0.64); 43 (0.15); 44 (2.06); 46 (0.0033); 48 (0.19)	39 (β^+, $1.06s$); 45 ($\beta^-\gamma$, $180d$); 49 ($\beta^-\gamma$, $2.5h$); 49 (β^-, $30m$)
Sc	21	45 (100)	41 (β^+, $0.87s$); 43 (β^+, $3.92h$); 44 ($IT\gamma$, $2.44d$); 44 ($\beta^+\gamma$, $3.9h$); 46 ($\beta\gamma$, $85d$); 47 ($\beta^-\gamma$, $63h$); 48 ($\beta^-\gamma$, $44h$); 49 (β^-, $57m$)
Ti	22	46 (7.95); 47 (7.75); 48 (73.5); 49 (5.51); 50 (5.34)	45 (β^+, $3.08h$); 45 (?, $21d$); 51 ($\beta^-\gamma$, $6m$); 51 ($\beta^-\gamma$, $72d$)
V	23	51 (100)	48 ($\beta^+\gamma$, $16d$); 49 (β^+, $33m$); 49 (K, $600d$); 50 (β^+, $3.7h$); 52 ($\beta^-\gamma$, $3.9m$)
Cr	24	50 (4.49); 52 (83.78); 53 (9.43); 54 (2.30)	49 ($\beta^+\gamma$, $42m$); 51 ($K\gamma C$, $26.5d$); 55 (?, $2h$)

[1] y = year, d = day, h = hour, m = minute, s = second

TABLE VI (*Continued*)

STABLE AND UNSTABLE ISOTOPES OF THE ELEMENTS

Element	At. No.	Stable Isotopes (Per Cent Abundance)	Radioactive Isotopes (Radiation; Half-life [1])
Mn	25	55 (100)	51 (β^+, 46*m*); 52 ($\beta^+\gamma$, 21*m*); ($\beta^+\gamma$, 6.5*d*); 54 ($K\gamma$, 310*d*); 56 ($\beta^-\gamma$, 2.59*h*)
Fe	26	54 (6.04); 56 (91.57); 57 (2.11); 58 (0.28)	53 (β^+, 8.9*m*); 55 (*KC*, 4*y*); 59 ($\beta^-\gamma$, 47*d*)
Co	27	59 (100)	55 ($\beta^+\gamma$, 18.2*h*); 56 ($\beta^+\gamma$, 72*d*); 57 ($\beta^+\gamma$, 270*d*); 60 ($\beta^-\gamma$, 5.3*y*); ($\beta^-\gamma$, 10.7*m*)
Ni	28	58 (67.4); 60 (26.7); 61 (1.2); 62 (3.8); 64 (0.88)	57 (β^+, 36*h*); 59 (β^+, 15.0*y*); 65 ($\beta^-\gamma$, 2.6*h*)
Cu	29	63 (70.13); 65 (29.87)	58 (β^+, 7.9*m*); 60 (β^+, 81*s*); 61 (β^+, 3.4*h*); 62 (β^+, 10.5*m*); 64 ($\beta^+\beta^-$, 12.8*h*); 66 (β^-, 5*m*)
Zn	30	64 (50.9); 66 (27.3); 67 (3.9); 68 (17.4); 70 (0.5)	63 (β^+, 38*m*); 65 ($\beta^+\gamma$, 250*d*); 69 (γ, 13.8*h*); (β^-, 57*m*); 72 ($\beta^-\gamma$, 49*h*); 73 (β^-, 2*m*)
Ga	31	69 (61.2); 71 (38.8)	64 (β^+, 48*m*); 65 (*KC*, 15*m*); 66 (β^+, 9.4*h*); 67 ($K\gamma C$, 83*h*); 68 (β^+, 68*m*); 70 ($\beta^-\gamma$, 20*m*); 72 ($\beta^-\gamma$, 14.1*h*); 73 (β^-, 5*h*); 74 (β^-, 9*d*)
Ge	32	70 (21.2); 72 (27.3); 73 (7.9); 74 (37.1); 76 (6.5)	71 (*KC*, 11*d*); (β^+, 40*h*); 75 ($\beta^-\gamma$, 89*m*); 77 ($\beta^-\gamma$, 12*h*); 78 ($\beta^-\gamma$, 2.2*h*)
As	33	75 (100)	72 (β^+, 26*h*); 73 (*KC*, 90*d*); (β^+, 50*h*); 74 ($\beta^-\beta^+\gamma$, 16*d*); 76 ($\beta^+\beta^-\gamma$, 26.8*h*); 77 (β^-, 40*h*); 78 ($\beta^-\gamma$, 80*m*); 81 (β^-, 10*m*)
Se	34	74 (0.9); 76 (9.5); 77 (8.3); 78 (24.0); 80 (48.0); 82 (9.3)	75 (γ, *C*, 115*d*); 81 (*IT*, *C*, 57*m*) (β^-, 19*m*); 83 ($\beta^-\gamma$, 30*m*); 84 (β^-, 2*m*)
Br	35	79 (50.6); 81 (49.4)	78 ($\beta^+\gamma$, 6.4*m*); 80 (*C*, 4.4*h*) ($\beta^-\gamma$, 18*m*); 82 ($\beta^-\gamma$, 34*h*); 83 (β^-, 140*m*); 84 (β^-, 33*m*); 85 (β^-, 3*m*); 87 (β^-, 50*s*)
Kr	36	78 (0.35); 80 (2.01); 82 (11.53); 83 (11.53); 84 (57.11); 86 (17.47)	79 (β^+, 34*h*); 81 (γ, 13*s*) (γ, 55*s*); 83 (*IT.C*, 113*m*); 85 ($\beta^-\gamma$, 4*s*) (β^-, 10*y*); 87 (β^-, 3*h*); 88 (β^-, 3*h*); 89 (β^-, 2.7*m*); 90 (β^-, 33*s*); 91 (β^-, 5.7*s*); 92 (β^-, 1.5*s*); 94 (1.4*s*); 95 (β^-, 2*s*); 97 (β^-, Short)

[1] *y* = year, *d* = day, *h* = hour, *m* = minute, *s* = second

TABLE VI (*Continued*)

STABLE AND UNSTABLE ISOTOPES OF THE ELEMENTS

Element	At. No.	Stable Isotopes (Per Cent Abundance)	Radioactive Isotopes (Radiation; Half-life [1])
Rb	37	85 (72.8); 87 (27.2)	86 ($\beta^-\gamma$, 19.5*d*); 87 ($\beta^-\gamma$, $6.3 \times 10^{10}y$); 88 (β^-, 17.5*m*); 89 ($\beta^-\gamma$, 15*m*); 90 (β^-, Short); 91 (β^-, Short); 92 (β^-, 80*s*); 94 (β^-, Short); 95 (β^-, Short); 97 (β^-, Short)
Sr	38	84 (0.56); 86 (9.86); 87 (7.02); 88 (82.56)	85 (γ, 65*d*) (γ, 70*m*); 87 (γ, 2.7*h*); 89 (β,$^-$ 55*d*); 90 (β^-, 25*y*); 91 ($\beta^-\gamma$, 9.7*h*); 92 (β^-, 2.7*h*); 94 (β^-, 7*m*); 95 (β^-, 2*m*); 97 (β^-, Short)
Y	39	89 (100)	86 (γ, 105*d*); 87 ($C\gamma$, 14*h*) (K, 80*h*); 88 (β^+, 20*h*); 90 (β^-, 60*h*); 91 (β^-, 57*d*) ($C\gamma$, 50*m*); 92 (γ, 3.5*h*); 94 (β^-, 20*m*); 95 ($\beta^-\gamma$, 11.5*h*); 97 (β^-, Short)
Zr	40	90 (48.0); 91 (11.5); 92 (22.0); 94 (17.0); 96 (1.5)	89 (β^+, 78*h*) ($C\gamma$, 4.5*m*); 93 (?, 2.5*m*); 95 ($\beta^-\gamma$, 65*d*); 97 ($\beta^-\gamma$, 17*h*); 98 (β^-, 18*m*) (β^-, 6*m*); (β^-, 70*h*)
Nb	41	93 (100)	90 (β^+, 21*h*); 91 (γ, 55*d*); 92 ($\beta^-\gamma$, 11*d*); 94 ($\beta^-\gamma$, 6.6*m*); 95 ($\beta^-\gamma$, 35*d*) (*IT*, *C*, 90*h*); 96 (?, 96*h*); 97 ($\beta^-\gamma$, 75*m*)
Mo	42	92 (14.9); 94 (9.4); 95 (16.1); 96 (16.6); 97 (9.65); 98 (24.1); 100 (9.25)	93 ($\beta^-\gamma$, 6.7*h*) (β^+, 17*m*); 99 ($\beta^-\gamma$, 67*h*); 101 ($\beta^-\gamma$, 14.6*m*); 102 (β^-, 12*m*); 105 (β^-, Short)
Tc	43		94 (K, 2*d*); 96 (K, 42*d*); 97 (*IT*, 90*d*); 98 (γ, 62*d*); 99 (γ, 6.6*h*) (β, 2×10^6y); 100 (β^-, 40*h*); 101 ($\beta\gamma$, 14*m*); 102 (β^-, 1*m*); 104 (γ, 110*h*); 105 (β^-, Short); 106 (β^-, 18*s*); 107 (β^-, 36.5*h*)
Ru	44	96 (5.68); 98 (2.22); 99 (12.81); 100 (12.70); 101 (16.98); 102 (31.34); 104 (18.27)	103 ($\beta^-\gamma$, 45*d*); 105 ($\beta^-\gamma$, 4*h*); 106 (β^-, 330*d*); 107 (β^-, 60*d*); 108 (β^-, 1.2*h*); 111 (β^-, 4*m*)

[1] y = year, d = day, h = hour, m = minute, s = second

TABLE VI (*Continued*)

STABLE AND UNSTABLE ISOTOPES OF THE ELEMENTS

Element	At. No.	Stable Isotopes (Per Cent Abundance)	Radioactive Isotopes (Radiation; Half-life [1])
Rh	45	103 (100)	102 ($\beta^-\beta^+\gamma$, 210*d*); 103 (*IT*, 53*m*); 104 (*ITC*, 4.2*m*) (β^-, 44*s*); 105 ($\beta^-\gamma$, 35*h*); 106 (β^-, 30*s*); 107 (β^-, 57*m*); 108 (β^-, 30*d*); 109 (β^-, 1*h*); 110 ($\beta^-\gamma$, 9*h*); 111 (β^-, 24*m*)
Pd	46	102 (0.8); 104 (9.3); 105 (22.6); 106 (27.2); 108 (26.8); 110 (13.5)	109 (β^-, 13*h*); 111 (β^-, 26*m*); 112 (β^-, 21*h*)
Ag	47	107 (51.9); 109 (48.1)	106 (β^+, 24.5*m*) (*KC*γ, 8.2*d*); 107 (*ITC*, 44*s*); 108 (β^-, 2.3*m*); 109 (*IT*γ, 40.5*s*); 110 (*K*γ*C*, 225*d*) ($\beta^-\gamma$, 22*s*); 111 (β^-, 7.5*d*); 112 ($\beta^-\gamma$, 3.2*h*)
Cd	48	106 (1.4); 108 (1.0); 110 (12.8); 111 (13.0); 112 (24.2); 113 (12.3); 114 (28.0); 116 (7.3)	107 (*K*γ, 6.7*h*) (*K*, 158*d*); 109 (β^+, 35*m*); 111 (*IT*, 48*m*); 115 ($\beta^-\gamma$, 2.33*d*) ($\beta^-\gamma$, 43*d*); 117 (β^-, 2.8*h*)
In	49	113 (4.5); 115 (95.5)	110 (β^+, 65*m*); 111 ($\beta^+\gamma$, 23*m*); 112 (*K*γ*C*, 2.7*d*) (*IT*γ*C*, 16.5*m*); 113 (*IT*γ*C*, 105*m*); 114 (*IT*γ*C*, 48*d*) (β^-, 72*s*); 115 (*IT*γ*C*, 4.5*h*); 116 (β^-, 13*s*) ($\beta^-\gamma$, 54*m*); 117 ($\beta^-\gamma$, 117*m*)
Sn	50	112 (1.1); 114 (0.8); 115 (0.4); 116 (15.5); 117 (9.1); 118 (22.5); 119 (9.8); 120 (28.5); 122 (5.5); 124 (6.8)	109 (β^-, 13*d*); 110 (β^-, 3*h*); 111 (β^-, 25*m*); 113 (*KC*γ, 90*d*); 121 (β^-, 40*m*); 123 (β^-, 26*h*); 125 (β^-, 9*m*); 126 (β^-, 62*h*); 127 ($\beta^-\gamma$, 10*d*); 128 (β^-, 20*m*); 129 ($\beta^-\gamma$, 70*m*)
Sb	51	121 (56); 123 (44)	116 (β^+, 3.6*m*); 120 (β^+, 17*m*); 122 ($\beta^-\gamma$, 2.8*d*); 124 ($\beta^-\gamma$, 60*d*); 125 (?, 2.7*y*); 126 (β^-, 3*h*) (?, 45*d*); 127 ($\beta^-\gamma$, 80*h*); 128 (β^-, 60*m*); 129 (β^-, 4.2*h*) 132 (β^-, 5*m*); 133 (β^-, 10*m*)

[1] *y* = year, *d* = day, *h* = hour, *m* = minute, *s* = second

TABLE VI (*Continued*)

STABLE AND UNSTABLE ISOTOPES OF THE ELEMENTS

Element	At. No.	Stable Isotopes (Per Cent Abundance)	Radioactive Isotopes (Radiation; Half-life [1])
Te	52	120 (0.09); 122 (2.43); 123 (0.85); 124 (4.59); 125 (6.93); 126 (18.71); 128 (31.86); 130 (34.52)	121 (K, 17d) (IT, 143d); 122 (ITC, 30d); 127 (ITC, 90d) (β^-, 9.3h); 129 (ITC, 32d) (β^-, 72m); 131 (ITC, 30h) (β^-, 25m); 132 ($\beta^-\gamma$, 77h); 133 (β^-, 60m); 134 (β^-, 43m); 135 (β^-, 2m); 136 (β^-, 1m)
I	53	127 (100)	124 (β^+, 4.0d); 126 ($\beta^-\gamma$, 13.0d); 128 ($\beta^-\gamma$, 25m); 130 ($\beta^-\gamma$, 12.6h); 131 ($\beta^-\gamma$, 8.0d); 132 ($\beta^-\gamma$, 2.4h); 133 ($\beta^-\gamma$, 22h); 134 ($\beta\gamma$, 54m); 135 ($\beta^-\gamma$, 6.7h); 137 (β^-, 22.5s)
Xe	54	124 (0.09); 126 (0.09); 128 (1.90); 129 (26.23); 130 (4.07); 131 (21.17); 132 (26.96); 134 (10.54); 136 (8.95)	127 ($IT\gamma$, 75s) ($IT\gamma$, 34d); 133 (β^-, 5.5d); 135 ($\beta^-\gamma$, 9.4h) ($\beta^-\gamma$, 15.6m); 137 (?, 68m) (β^-, 3.4m); 138 (β^-, 17m); 139 (β^-, 41s); 140 (β^-, 16s); 141 (β^-, 1.7s); 142 (β^-, 1.3s); 143 (β^-, 0.5s) (β^-, Short)
Cs	55	133 (100)	130 (?, 30m); 132 (γ, 7.1d); 134 (β^-, 3h) ($\beta^-\gamma$, 1.7y); 135 (β^-, 2.5 $\times$ 10^4y); 136 ($\beta^-\gamma$, 10.5d); 137 ($\beta^-\gamma$, 27y); 138 ($\beta\gamma$, 33m); 139 (β^-, 7m); 140 (β^-, 40s); 141 (β^-, Short); 142 (β^-, 1m); 143 (β^-, Short); 144 (—, Short); 145 (β^-, Short)
Ba	56	130 (0.10); 132 (0.09); 134 (2.42); 135 (6.59); 136 (7.81); 137 (11.32); 138 (71.66)	133 ($IT\gamma$, 38.8h); 139 ($\beta^-\gamma$, 86m) 140 ($\beta^-\gamma$, 12.5d); 141 (β^-, 18m); 142 (β^-, 6m); 143 (β^-, 0.5m); 144 (β^-, 1m); 145 (β^-, Short)

[1] y = year, d = day, h = hour, m = minute, s = second

TABLE VI (*Continued*)

STABLE AND UNSTABLE ISOTOPES OF THE ELEMENTS

Element	At. No.	Stable Isotopes (Per Cent Abundance)	Radioactive Isotopes (Radiation; Half-life [1])
La	57	139 (100)	137 ($K\gamma$, 17.5h); 140 (β^-, 40h); 141 (β^-, 3.5h); 142 ($\beta^-\gamma$, 74m); 143 (β^-, 20m); 144 (β^-, Short); 145 (β^-, Short)
Ce	58	136 (<1); 138 (<1); 140 (89); 142 (11)	140 ($IT\gamma$, 140d); 141 (β^-, 30d); 143 (β^-, 36h); 144 ($\beta^-\gamma$, 275d); 145 (β^-, 1.8h); 146 (β^-, 14.6m)
Pr	59	141 (100)	140 (β^+, 3.5m); 142 ($\beta^-\gamma$, 19.3h); 143 (β^-, 13.5d); 144 (β^-, 17m); 145 (β^-, 4.5h); 146 ($\beta^-\gamma$, 24.6m)
Nd	60	142 (25.95); 143 (13.0); 144 (22.6); 145 (9.2); 146 (16.5); 148 (6 8); 150 (5.95)	141 (β^+, 2.5h); 147 ($\beta^-\gamma$, 11.0d); 149 ($\beta^-\gamma$, 17h)
Pm	61		143 (β^-, 12.5h); 147 (β^-, 4y); 148 ($\beta^-\gamma$, 2.7h); 149 ($\beta^-\gamma$, 47h); 151 (β^-, 12m)
Sm	62	144 (3); 147 (16.1); 148 (14.2); 149 (15.5); 150 (11.6); 152 (20.7); 154 (18.9)	151 (β^-,Long); 153 (IT, 46h); 155 (β^-, 21m); 156 (β^-, 10h)
Eu	63	151 (49.1); 153 (50.9)	150 (β^+, 27h); 152 ($\beta\gamma$, 9.2h); 154 ($\beta^-\gamma$, 7y); 155 ($\beta^-\gamma$, 2y); 156 ($\beta^-\gamma$, 15.4d); 157 (β^-, 15.4d); 158 (β^-, 60m)
Gd	64	152 (0.2); 154 (1.5); 155 (18.4); 156 (19.9); 157 (18.9); 158 (20.9); 160 (20.2)	
Tb	65	159 (100)	160 (β^-, 3.9h) ($\beta^-\gamma$, 72d)
Dy	66	158 (0.1); 160 (0.1); 162 (26.6); 163 (24.8); 164 (27.3)	163 (ITC, 1.2m); 165 ($\beta^-\gamma$, 2.5h)
Ho	67	165 (100)	164 (β^+, 47m); 166 (β^-, 35h)
Er	68	162 (0.1); 164 (1.5); 166 (32.9); 167 (24.4); 168 (26.9); 170 (14.2)	165 (β^-, 1.1m); 169 (β^-, 7m) (β^-, 12h)
Tm	69	169 (100)	170 (?, 105d)
Yb	70	168 (0.06); 170 (4.21); 171 (14.26); 172 (21.49); 173 (17.02); 174 (29.58); 176 (13.38)	175 (β^-, 4.2h) (β^-, 45d)
Lu	71	175 (97.5); 176 (2.5)	176 ($\beta^-\gamma$, 3.7h); 177 (β^-, 6.6d)
Hf	72	174 (0.18); 176 (5.3); 177 (18.47); 178 (27.1); 179 (13.85); 180 (35.11)	179 (ITC, 19s); 181 (β^-, 55d)

[1] y = year, d = day, h = hour, m = minute, s = second

TABLE VI (*Continued*)

STABLE AND UNSTABLE ISOTOPES OF THE ELEMENTS

Element	At. No.	Stable Isotopes (Per Cent Abundance)	Radioactive Isotopes (Radiation; Half-life [1])
Ta	73	181 (100)	180 (?, 18*m*) ($K\gamma\beta^-$, 8.2*h*); 182 ($\beta^-\gamma$, 120*d*) ($\beta^-\gamma$, 16.2*m*)
W	74	180 (0.2); 182 (22.6); 183 (17.3); 184 (30.1); 186 (29.8)	185 ($\beta^-\gamma$, 77*d*); 187 ($\beta^-\gamma$, 24.1*h*)
Re	75	185 (38.2); 187 (61.8)	182 (β^+, 40*m*); 184 ($K\gamma$, 52*d*); 186 (β^-, 90*h*); 188 ($\beta^-\gamma$, 18*h*)
Os	76	184 (0.02); 186 (1.59); 187 (1.64); 188 (13.3); 189 (16.1); 190 (26.4); 192 (41.0)	185 (β, 30*h*) ($IT\gamma$, 99*d*); 191 ($\beta^-\gamma$, 32*h*); 193 ($\beta^-\gamma$, 17*d*)
Ir	77	191 (38.5); 193 (61.5)	190 ($\gamma\beta^+$, 9.4*d*); 192 (β^-, 15*m*); ($\beta^-\gamma$, 68*d*); 194 ($\beta^-\gamma$, 19*h*)
Pt	78	192 (0.8); 194 (30.2); 195 (35.3); 196 (26.6); 198 (7.2)	196 (*ITC*, 80*m*); 197 (β^-, 18*h*); ($\beta^-\gamma$, 3.3*d*); 199 (β^-, 31*m*)
Au	79	197 (100)	196 (β^-, 13*h*) ($\beta^-\gamma$, 5.6*d*); 197 (*IT*, 7*s*); 198 ($\beta^-\gamma$, 2.7*d*); 199 ($\beta^-\gamma$, 3.3*d*); 200 (β^-, 48*m*)
Hg	80	196 (0.15); 198 (10.1); 199 (17.0); 200 (23.3); 201 (13.2); 202 (29.6); 204 (6.7)	197 (γ^-, 23*h*) (γ, 64*h*); 199 (γ, 43*m*); 203 ($\beta^-\gamma$, 51.5*d*); 205 (β^-, 5.5*m*)
Tl	81	203 (29.1); 205 (70.9)	198 ($K\gamma$, 10.5*h*); 199 (*C*, 44*h*); 201 (?, 3.8*h*) (?, 4*m*); 202 (γ, 13*d*); 204 (β^-, 3.5*y*); 206 (β^-, 4.23*m*); 207 ($\beta^-\gamma$, 4.76*m*); 208 ($\beta^-\gamma$, 3.1*m*); 209 (β^-, 1*h*); 210 (β^-, 1.32*m*)
Pb	82	204 (1.5); 206 (23.6); 207 (22.6); 208 (52.3)	203 (*K*, *IT*, 54*h*); 205 ($IT\gamma$, 68*m*); 209 (β^-, 3.3*h*); 210 (β, 22*y*); 211 ($\beta^-\gamma$, 36.1*m*); 212 (β^-, 10.6*h*); 214 ($\beta^-\gamma$, 26.8*m*); 215 ($IT\gamma$, 1.6*m*)
Bi	83	209 (100)	205 ($K\gamma$, 12*h*); 206 ($KC\gamma$, 6.4*d*); 208 ($K\beta\gamma$, 10^4*y*); 210 (β^-, 5.0*d*); 211 ($\beta^-\gamma$, 216*m*); 212 ($\gamma\beta^-$, 60.5*m*); 214 ($\alpha\beta^-\gamma$, 19.7*m*)

[1] *y* = year, *d* = day, *h* = hour, *m* = minute, *s* = second

TABLE VI (*Continued*)

STABLE AND UNSTABLE ISOTOPES OF THE ELEMENTS

Element	At. No.	Stable Isotopes (Per Cent Abundance)	Radioactive Isotopes (Radiation; Half-life [1])
Po	84		206 ($K\alpha\gamma$, 11d); 207 (K, 5.7h); 208 (α, 4y); 210 ($\alpha\gamma$, 140d); 211 (α, $5 \times 10^{-3}s$); 212 (α, $3 \times 10^{-7}s$); 213 (α, $70^{-6}s$); 214 (α, $1.5 \times 10^{-4}s$); 215 (α, $1.83 \times 10^{-3}s$); 216 ($\alpha\beta^-$, $1.58 \times 10^{-1}s$); 218 ($\alpha\beta^-$, 3.05m)
At	85		211 (αK, 7.5h)
Rn	86		219 (α, 3.92s); 220 (α, 54.5s); 221 (α, 1h); 222 (α, 3.825d)
Fr	87		223 ($\beta^-\gamma$, 21m)
Ra	88		222 (α, 0.5m); 223 ($\alpha\gamma$, 11.2d); 224 (α, 3.64d); 226 ($\alpha\gamma$, 1590y); 228 (β, 6.7y)
Ac	89		227 ($\alpha\beta^-$, 13.5y); 228 (?, 6.13h)
Th	90	232 (100)	227 ($\alpha\gamma$, 18.9d); 228 ($\alpha\gamma$, 1.90y); 230 ($\alpha\gamma$, 8.3×10^4y); 231 (β^-, 24.6h); 233 (β^-, 23m); 234 ($\beta^-\gamma$, 24.5d)
Pa	91		231 ($\alpha\gamma$, 3.2×10^4y); 233 ($\beta^-\gamma$, 27.4d); 232 ($\beta^-\gamma$, 6.7h) ($\beta\gamma$, 1.14m)
U	92	238 (99.274); 235 (0.719); 234 (0.005)	234 (α, 2.33×10^5y); 235 (α, 7.07×10^8y); 237 ($\beta^-\gamma$, 6.8d); 238 (α, 4.51×10^9y); 239 (β^-, 23m)
Np	93		235 (K, 250d); 236 (β^-, 20h); 237 (α, 2.25×10^6y); 238 (β^-, 2d); 239 ($\beta^-\gamma$, 2.3d)
Pu	94		238 (?, 50y); 239 (α, 24,000y)
Am	95		241 (α, 500y)
Cm	96		240 (α, 30d); 242 (α, 150d)

[1] y = year, d = day, h = hour, m = minute, s = second

The Einstein Equation—The Packing Fraction. In experiments such as shown in Fig. 146 at ordinary voltages the velocity of the electron is less than 10^9 cm per second, and the value of e/m is independent of the velocity. As the velocity is increased, however, and approaches the velocity of light, the value of e/m increases in accordance with the theory of relativity. The actual mass m of a particle is related to the "rest mass" m_0 and the velocity v by the equation,

$$m = \frac{m_0}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

where c is the velocity of light.

Differentiating this equation and applying the relations that force is the rate of change of momentum, and that kinetic energy is force acting through a distance, one can show that

$$dE = c^2 dm$$

Einstein in 1906 proposed this epoch-making theory according to which

$$E = c^2 m \tag{12}$$

and pointed out that the annihilation of 1 g of matter will produce $(2.99 \times 10^{10})^2$ or 8.988×10^{20} ergs of energy.

In the nuclear reaction,

$$2 \text{ protons} + 2 \text{ neutrons} \rightarrow 1 \text{ alpha particle}$$

$$2 \times 1.007582 + 2 \times 1.00893 \rightarrow 4.002763$$

there is an actual loss of mass of $(4.002763 - 4.03302) = -0.03026$. If the Einstein equation is applied, the formation of a mole of alpha particles or helium nuclei from neutrons and protons evolves $0.03026 \times 8.988 \times 10^{20}$ ergs or 6.5×10^{11} cal. This nuclear energy is many orders of magnitude greater than chemical energy produced by changes of atoms to give different molecules.

The loss of mass which is produced by the formation of atomic nuclei from protons and neutrons applies to other nuclei as well as the nucleus of helium and is called the packing effect.

The *packing fraction* is defined as the difference between the actual mass of the isotope and the nearest whole number divided by this mass number. Thus, the mass of one of the chlorine isotopes is 34.983, and the packing fraction is $(34.983 - 35.000)/35.000 = -0.00048$. Packing fractions are usually expressed in parts per 10,000, and so the pack-

ing fraction of chlorine is written −4.8. Since oxygen is taken as the standard, elements with positive packing fractions are less stable than oxygen; those with negative packing fractions are more stable. The elements in the middle range of the periodic table seem to be the most stable, the light elements and the heavy elements possessing positive packing fractions.

The condensation of hydrogen to helium and of other light elements to give heavier ones with the attendant loss of mass is the explanation for the radiant heat given off by the sun and the stars. There appears to be no chance, however, that atomic energy can be obtained on earth by the condensation of the nuclei of light elements because a temperature of many millions of degrees is required.

The breakdown of atomic nuclei results in an actual loss of mass and evolution of energy. In all nuclear reactions such as those discussed in the preceding section, the total loss of mass enables one to calculate accurately the energies produced. The energies of alpha and beta particles and of gamma rays can be determined in this way; or the velocities can be determined by measuring their penetration of sheets of metal, and from these data the loss of mass can be determined. Again a knowledge of the atomic masses enables one to calculate the accelerating voltage which must be applied in order to bring about a specified nuclear reaction.

Nuclear Fission. In 1939 Hahn and Strassman exposed uranium to neutrons and obtained unexpected products which were identified as barium and other elements of the middle of the periodic table. Meitner interpreted this nuclear reaction as a complete breakdown of the uranium atom into two elements of approximately half the atomic weight of uranium. This new phenomenon was called fission and led immediately to a large number of confirming experiments in many different laboratories throughout the world. It was soon found that it is the isotope of uranium U^{235} which undergoes fission when it absorbs neutrons. The equation for this fission process is

$$n + U^{235} \rightarrow \begin{cases} \text{Kr} + \text{Ba} + \begin{cases} n + U^{235} \rightarrow \text{fission products} + \begin{cases} n \\ n \end{cases} \\ n + U^{235} \rightarrow \text{fission products} + \begin{cases} n \\ n \end{cases} \end{cases} \\ \text{etc.} \end{cases}$$

In this nuclear reaction Kr and Ba are representative of a large number of possible middleweight elements, and the number of neutrons produced is not exactly two.

There are two remarkable things about nuclear fission. First, it is chain-reacting, so that the neutrons from the fission of the first atom

cause other uranium atoms to undergo fission and produce more neutrons in an instantaneous, expanding process. Second, the sum of all the masses of the elements and the neutrons produced in fission is slightly less than the sum of the masses of the original U^{235} plus the original neutron. It was evident at once that here might be a source of atomic energy on a large scale, because, once the reaction was started with a neutron, the process might be self-sustaining, and the loss of mass in the reaction would lead, of necessity, to the evolution of enormous quantities of energy. Previous considerations for producing useful atomic

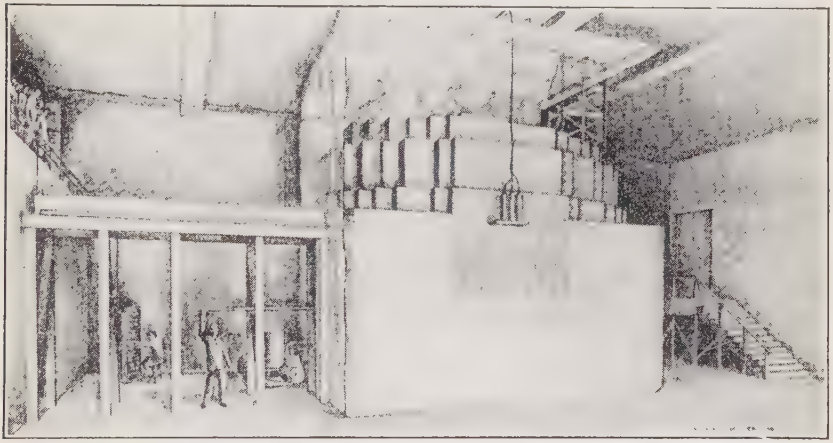


Fig. 158. First nuclear chain-reacting pile.

energy would have required the expenditure of large quantities of energy in a cyclotron or other device to sustain the nuclear reaction. Fission, however, might be a process which would run spontaneously without the investment of large amounts of energy.

On December 2, 1942, the first test of this idea was carried out by Fermi, Szillard, Wigner, and others under the administration of A. H. Compton, at the University of Chicago. The experiment, pictured in **Fig. 158,** was successful in proving that it is possible to obtain a controlled, self-sustaining chain reaction. It was necessary to obtain uranium in a high state of purity and to imbed it in graphite of high purity. The graphite acted as a moderator to slow down the neutrons to such a velocity that they would be more easily captured by the surrounding uranium. This self-sustaining nuclear reactor is called a "pile." Instead of the graphite moderator light elements like deuterium and beryllium can be used as they do not absorb neutrons.

These piles supply not only large quantities of heat but also an excess of neutrons which can be used for the transmutation of elements.

When neutrons are absorbed by uranium 238, the following nuclear reactions take place:

$$_{92}U^{238} + n \rightarrow {}_{92}U^{239}; \qquad {}_{92}U^{239} \rightarrow {}_{93}Np^{239} + \beta^{-};$$

$$_{93}Np^{239} \rightarrow {}_{94}Pu^{239} + \beta^{-}$$

Plutonium 239 undergoes fission in the same manner as uranium 235. Uranium 233 which also undergoes fission can be produced from nuclear reactions starting with the action of neutrons on thorium.

The rate at which this fission process takes place in a pile can be controlled easily with the help of rods of cadmium- or boron-containing material or other material which has great absorption for neutrons. When the rods are inserted into the pile, the chain reaction cannot continue, because the neutrons are absorbed by the rods. By pulling out the rods the absorption of the neutrons in the pile is decreased, so that by proper mechanical regulation the pile may be made to develop heat at any rate desired, limited only by the rate at which heat can be removed from the pile. The accumulation of too much heat will endanger the materials of which the pile is constructed. Several atomic piles are now in operation, all at comparatively low temperatures. It is possible, however, to operate other piles at a much higher temperature and to utilize the heat removed for the operation of heat engines or turbines which can be used to produce useful electricity.

In the future it is expected that standard power plants will be operated by atomic fuel, but the large capital investment for the fissionable material and the pile, together with the special difficulties due to radioactivity, makes it appear that electricity generated by atomic power will not be cheaper in most countries than the electricity generated by the burning of coal. There are certain considerations, however, which are of special interest. If 1 g of uranium 235 undergoes complete fission, the loss in mass will result in the evolution of 2×10^{10} cal. If this is compared with chemical reactions, the combustion of 1 g of carbon evolves 7,870 cal of heat. One pound of uranium 235 will generate as much heat on fission as is generated by the burning of 1500 tons of coal, equivalent to 11 million kilowatt-hours of heat or, at present turbine efficiencies, to about 3 million kilowatt-hours of electricity. Accordingly, atomic fuel may be essentially regarded as weightless fuel and may well find its first practical applications in isolated regions where coal and other fuel are not now available and transportation is difficult.

A certain critical amount of U^{235} or other fissionable material is necessary before the pile can be self-sustaining. With lesser amounts a sufficiently large number of neutrons escape from the pile so that the

nuclear chain is no longer self-propagating. This critical size involves an investment of such a large amount of material and the nuclear reactor requires such a heavy protecting shield that small units for the produc-

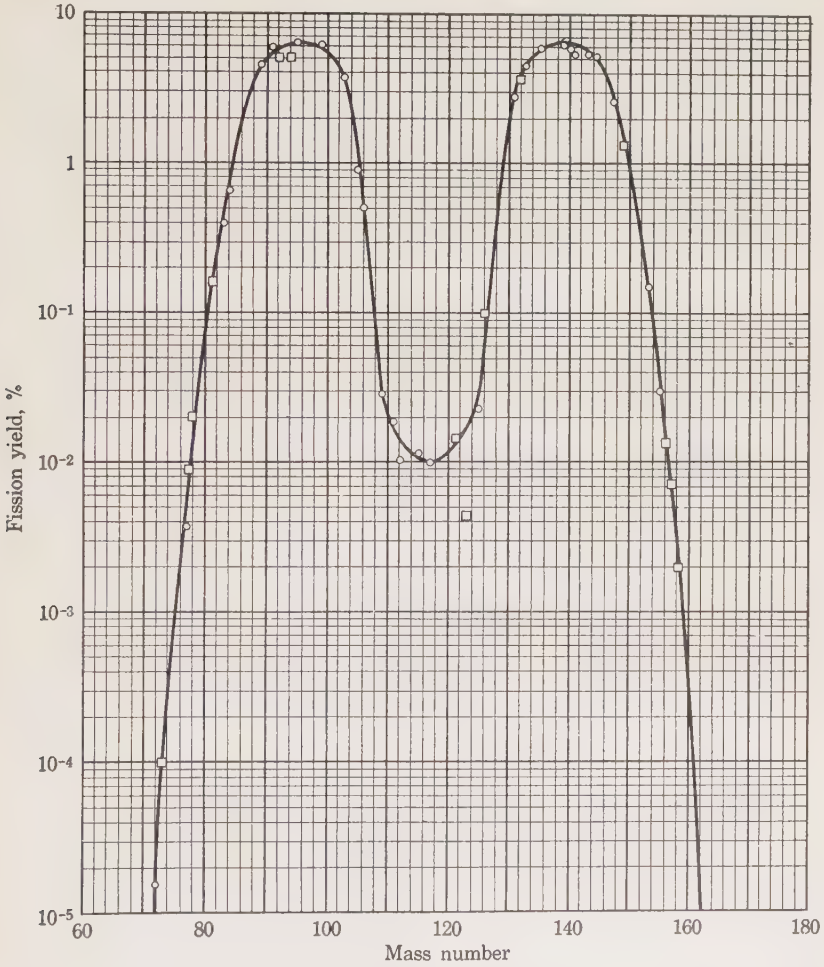


FIG. 159. Distribution of fission products. ○ certain mass assignment. □ uncertain mass assignment.

tion of power or heat will not be practical. It is expected that ships will be operated by atomic fuel but that automobiles cannot be. The widespread use of atomic power will probably have to come slowly until a strong international organization is established, because the atomic fuel in power piles can be misused for military purposes; hence, world-wide regulation is necessary.

The distribution of elements produced in fission shows a probability pattern as given in **Fig. 159.*** The logarithms of the percentage yield are plotted as ordinates against the atomic masses.

When U^{235} undergoes fission, all the elements between zinc with an atomic number of 30 and gadolinium with an atomic number of 64 are produced, including about 300 isotopes, most of which are radioactive with half-lives ranging from fractions of a second to many years. The fission products do not emit alpha particles, and the majority emit beta or gamma rays. There are about eight different isotopes, including some of strontium, barium, and iodine, each of which accounts for as much as 5 per cent of the original weight of the uranium.

The piles supply large quantities of neutrons which can be used for experimental studies and for the production of many useful isotopes, as, for example, radioactive carbon C^{14} from nitrogen. A catalogue is now available which lists the many different isotopes which can be obtained at a nominal price from the U. S. Atomic Energy Commission, at Oak Ridge, Tenn.

Beams of neutrons from the pile are of value for certain physical measurements. They can, for example, be used like beams of electrons and X rays in the study of crystal and molecular structure.

The energy evolved in the fission of U^{235} is of the order of 2 to 6 million electron volts. The cyclotron at California with 200 million electron volts has been able to cause the fission of many heavy elements such as lead. The pattern of distribution of the lighter elements produced differs from that shown in Fig. 159 in that the base is broader and the peaks are lower. These disintegrations produced with the common heavy elements are not chain reacting and will not continue to produce energy when the exciting energy is removed.

Biological Effects of Radioactivity. Serious damage can be done to living tissue by excessive exposure to radioactivity. The exact nature of these reactions is not fully understood, but the ionizing radiations may produce hydrogen peroxide and other chemical substances which then react chemically with the material of the cells. As a rough approximation, the effect of X rays, gamma rays, beta rays, alpha particles, and neutrons is proportional to the amount of ionization which these various agents can produce. The biological effect can be thus correlated with the intensity of radiation of the various types as measured by physical instruments, such as photographic plates, ionization chambers, and Geiger–Müller counters.

Fortunately, these instruments are so sensitive to radioactivity that they give an adequate measure of the radiation at most levels long before

* Plutonium Project, *J. Am. Chem. Soc.*, **68**, 2411 (1946).

any biological damage can be expected. As a matter of fact, the limitation to the Geiger–Müller counters is usually the background of ionization produced by cosmic rays, and all living matter is and always has been exposed to these cosmic rays. Considerable study has been devoted to establishing a safe limit for exposure to X rays and radioactivity. Overexposure to radioactivity may cause severe burns which heal very slowly. Even though no immediate effect appears, difficulties may appear years later. In the more severe cases the concentration of red blood cells is reduced through destructive action on material in the bone marrow, and testing red-blood-count corpuscles is a standard procedure in checking for overexposure to radioactivity. Exposure to neutrons leads to effects which are quite similar to the exposure to gamma rays or beta or alpha particles, because the neutrons are absorbed by the nuclei of sodium and other elements in the living body with the production of radioactive isotopes.

Those who work with radioactive materials must guard themselves against damage from exposure to radioactivity. The gamma rays are stopped by shields of sheet lead or by walls of interlocking bricks of lead. Concrete is also used. For gamma rays the stopping power of the shield material depends on the thickness and density of the material. Sometimes gloves containing lead are used to protect the hands. Neutrons are stopped by paraffin or other hydrogen-containing material and by cadmium sheets or boron-containing material. Alpha particles are stopped by thin walls of glass or any type of shield. Beta rays require somewhat thicker glass. It is necessary to guard against dust particles of radioactive material, because tiny particles of material which are radioactive must be kept out of the lungs, the stomach, and the blood stream.

These hazards call for special shielding, ventilation, and waste disposal, and frequently lead to the requirement of remote control for laboratory experiments, but the techniques have been fully worked out, and there need be no danger if the precautions are followed and there is adequate monitoring of the laboratory with instruments suitable for detecting radioactivity.

Uses of Isotopes. Many uses had been developed for the naturally occurring radioactive elements (from lead to uranium in the periodic table), but the new artificially produced radioactivity has greatly increased the interest in this work because radioactive forms of almost any element can now be obtained.

The medical uses of radioactivity are well known. Although serious burns can be produced by radium, it is possible under properly controlled conditions to destroy early cancerous tissue and other abnormal

growths without serious injury to the normal flesh. For such purposes radon is used sealed off in small glass tubes. Radioactive cobalt produced by neutrons from a nuclear pile will probably find use in this field. Other radioactive elements may find therapeutic uses. Radioactive iodine is concentrated in the thyroid gland and is being used successfully in the cure of certain types of goiter.

Several applications of radioactivity have been made to geology.* One of the earliest was the determination of the age of the earth. The rates of radio disintegration are well established, and the age of a given uranium or other radioactive mineral is obtained by simply dividing the amount of disintegration product by the rate at which the product is generated. If the life of the parent element is very long, the calculations are simplified. The amount of lead found in a uranium mineral is a measure of the amount of uranium which has undergone radioactive disintegration, provided that no lead has been brought from other places and none has been leached out. A determination of the atomic weight or a measurement of the relative distribution of isotopes can be used to correct for any ordinary lead present which did not come from the uranium or thorium in the sample of mineral. The accumulation of helium from alpha particles is used also for dating minerals. The earth must be at least as old as the oldest mineral which is found, and several have been established to be about a billion years old.

Example 4. A sample of pitchblende was found to contain 51.16 per cent uranium and 2.492 per cent lead, giving a lead–uranium ratio of 0.0487.† An atomic weight determination showed that, whereas most of the lead came from uranium and had an atomic weight of 206, some ordinary lead was present, requiring a correction of Pb/U to 0.0453. The disintegration constant for uranium is 1.52×10^{-10} year $^{-1}$. How old must this mineral have been in order to accumulate this much lead?

$$\text{Ratio } \frac{U_{\text{disintegrated}}}{U_{\text{unchanged}}} = 0.0453 \times \frac{\text{At. wt. U}}{\text{At. wt. Pb}} = 0.0453 \times \frac{238}{206} = 0.0523$$

$$\frac{-dc}{dt} = kc$$

$$\frac{-0.0523}{dt} = 1.52 \times 10^{-10} \times 1$$

$$dt = 300 \text{ million years}$$

* Goodman, Geological Applications of Nuclear Physics, *J. Applied Phys.*, **13**, 276 (1942).

† Baxter and Averill, *J. Am. Chem. Soc.*, **59**, 705 (1937).

This is an approximate calculation assuming that for this problem 300 million years are infinitesimal! A more exact calculation may be made readily, thus:

$$1.52 \times 10^{-10} = \frac{2.303}{t} \log \frac{1.000}{1.000 - 0.0525}$$

The use of radio indicators offers a solution for certain analytical problems. The test for radioactivity is so much more sensitive than other physical or chemical tests that the minutest amount of material can be detected. The solubility of a difficultly soluble lead salt may be determined by placing a trace of radio lead in a saturated solution and allowing the radio lead to distribute itself between the solution and the solid. The distribution ratio can be easily and accurately determined by measuring the intensity of radioactivity. Again, it is possible with radio indicators to determine the actual number of atoms of lead or other elements exposed in a crystal, and, accordingly, the absolute surface can be calculated.

The use of isotopes as tracers is furnishing an important means for studying the mechanism of biological processes and chemical reactions.* For example, radioactive iodine and bromine have been used to follow the course of the halogen in organic reactions, and radioactive manganese has been used to show that there is no interchange of manganese between the ions of different valence, as, for example, between MnO_4^- and Mn^{++}, but that there is a rapid exchange between manganous ion and manganic oxalate ion.

By feeding radioactive phosphorus to a colony of rats and determining the radioactivity of the bone ash at frequent intervals, Hevesy found that a given atom of phosphorus remains in the bones only about a month, a fact which proved the hypothesis that the bones of a living animal are in a state of dynamic equilibrium with their surroundings. Radioactive phosphorus has been used also to determine the time required for inorganic phosphorus in the food to be converted into organic phosphorus material in the blood of rats.

Radioactive carbon C^{14} with a half-life of 4700 years is being widely used as a tracer in many biochemical, chemical, and industrial laboratories. One of the most important uses of radioactive carbon is in the study of photosynthesis, the process by which carbon dioxide and water are combined in the growing plants through the agency of sunlight. A method is now available for studying the first immediate products.

* "Isotopic Tracers in Biology and Medicine," University of Wisconsin Press, Madison, Wis. (1948); Shoenheimer, "Dynamic State of Body Constituents," Harvard University Press, Cambridge, Mass., 1942.

The stable isotopes as well as the radioactive isotopes are finding extensive use as tracers.

Deuterium, heavy carbon, and heavy oxygen have been used effectively as tracer elements in physical-chemical and biochemical investigations. The positions in a molecule or an organism taken by these tagged atoms can be ascertained with the help of a mass spectrometer which gives the ratio of the heavy isotope to the common isotope. For example, previously unavailable information has been found with the help of N^{15}, concerning the biochemical behavior of certain amino acids and proteins.

Many uses have been developed for deuterium, but, thus far, they have been restricted to the laboratory. Its use as a projectile in nuclear disintegrations has been stressed already. By substituting deuterium for hydrogen large band shifts are produced, and it is thus possible to connect spectral bands with definite bonds in the molecule. A large variety of new organic compounds has been synthesized in which deuterium takes the place of hydrogen. In one of the first tracer experiments ordinary sugar was dissolved in heavy water and the water distilled off. The density of this water was less than before, showing that some of the deuterium of the water had exchanged with hydrogen of the sugar. Quantitative measurements showed that half the hydrogen atoms of the sugar had exchanged with deuterium. It is known from the structure of sugar that half the hydrogens are attached to carbon and half to oxygen. It is concluded that those hydrogen atoms attached to oxygen ionize and mix with the deuterium ions of the water, but that the hydrogen atoms attached directly to carbon do not ionize and are unable to leave the sugar molecule.

Gold has been transmuted into Hg^{198}, through long exposure to neutrons in the pile by the reaction:

$$Au^{197} + n = Hg^{198}$$

The platinum–iridium bar at Paris has been accepted as the world's standard unit of length, but it is not sufficiently precise for some purposes; therefore, the red spectroscopic line of cadmium has been widely used. The green mercury line would be a better standard, because the heavier metal leads to a lower temperature of excitation with a line about half as wide as the cadmium line. But, ordinary mercury cannot be used because it contains seven isotopes each with a slightly different spectral line. However, 60 mg of mercury transmuted from gold has been distilled out and, being free from other isotopes, gives a very convenient narrow line at 5461 A which will perhaps be determined

TABLE VII

Periodic Classification of the Elements

Numbers above symbols are atomic numbers. Small numbers refer to electrons; those marked ‡ are filled shells of each period; those below each symbol indicate remaining electrons.

	Outer Shell	Group Ia	Group IIa	Groups → IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	Groups → IIIb	IVb	Vb	VIb	VIIb	Group O Inert Gases
				Transition Elements															
Period 1 2 elements	*K*	1 H 1																	2 He 2
Period 2 8 elements 2 ‡	*L*	3 Li 1	4 Be 2											5 B 3	6 C 4	7 N 5	8 O 6	9 F 7	10 Ne 8
Period 3 8 elements 2, 8 ‡	*M*	11 Na 1	12 Mg 2											13 Al 3	14 Si 4	15 P 5	16 S 6	17 Cl 7	18 A 8
Period 4 18 elements 2, 8 ‡	*N*	19 K 8, 1	20 Ca 8, 2	21 Sc 9, 2	22 Ti 10, 2	23 V 11, 2	24 Cr 13, 1	25 Mn 13, 2	26 Fe 14, 2	27 Co 15, 2	28 Ni 16, 2	29 Cu 18, 1	30 Zn 18, 2	31 Ga 18, 3	32 Ge 18, 4	33 As 18, 5	34 Se 18, 6	35 Br 18, 7	36 Kr 18, 8
Period 5 18 elements 2 8, 18 ‡	*O*	37 Rb 8, 1	38 Sr 8, 2	39 Y 9, 2	40 Zr 10, 2	41 Cb 12, 1	42 Mo 13, 1	43 Tc 13, 2	44 Ru 15, 1	45 Rh 16, 1	46 Pd 18, 0	47 Ag 18, 1	48 Cd 18, 2	49 In 18, 3	50 Sn 18, 4	51 Sb 18, 5	52 Te 18, 6	53 I 18, 7	54 Xe 18, 8
Period 6 32 elements 2, 8, 18 ‡	*P*	55 Cs 18, 8, 1	56 Ba 18, 8, 2	57–71 Rare Earths	72 Hf 32, 10, 2	73 Ta 32, 11, 2	74 W 32, 12, 2	75 Re 32, 13, 2	76 Os 32, 14, 2	77 Ir 32, 17, 0	78 Pt 32, 17, 1	79 Au 32, 18, 1	80 Hg 32, 18, 2	81 Tl 32, 18, 3	82 Pb 32, 18, 4	83 Bi 32, 18, 5	84 Po 32, 18, 6	85 At 32, 18, 7	86 Rn 32, 18, 8
Period 7 2, 8, 18, 32 ‡	*Q*	87 Fr 18, 8, 1	88 Ra 18, 8, 2	89–96 Actinides	→														

Actinide series IIIa 2, 8, 18, 32 ‡	89 Ac 18 9, 2	90 Th 19, 9, 2	91 Pa 20, 9, 2	92 U 21, 9, 2	93 Np 22, 9, 2	94 Pu 23, 9, 2	95 Am 24, 9, 2	96 Cm 25, 9, 2		

Rare-earth elements (Lanthanide series) IIIa 2, 8, 18 ‡	57 La 18, 9, 2	58 Ce 20, 8, 2	59 Pr 21, 8, 2	60 Nd 22 8, 2	61 Pm 23, 8, 2	62 Sm 24, 8, 2	63 Eu 25, 8, 2	64 Gd 25, 9, 2	65 Tb 27, 8, 2	66 Dy 28, 8, 2	67 Ho 29, 8, 2	68 Er 30, 8, 2	69 Tm 31, 8, 2	70 Yb 32, 8, 2	71 Lu 32, 9, 2

with an accuracy of one part in a billion and will probably become the primary standard of length.

Definition of Units of Radioactivity. The *curie* of radioactivity is now defined as that quantity of radioactive material in which there are 3.7×10^{10} disintegrations per second. Radioactive elements used in laboratory work are described in terms of their rates of disintegration; thus, a microcurie of radon, or radioactive carbon, or radioactive sodium will each give 37,000 disintegrations per second. The weakest radioactivity that can be measured under ordinary conditions is about 1 disintegration per second. The natural background of radioactivity due in part to cosmic rays is the limiting factor in some measurements.

The *roentgen* is the unit of radiation used for X rays or gamma rays, and it is defined in terms of the ionization produced in gases. One roentgen will produce one *electrostatic* unit of charge per cubic centimeter of air at standard conditions. It produces 2.083×10^9 pairs of gaseous ions in air per cubic centimeter under standard conditions and generates 83.3 ergs per gram of air. The intensity of gamma radiation (or X rays) obviously is decreased as one moves away from the source or interposes shields. For a typical gamma radiation the passage through 1 cm of lead will reduce the intensity by half. For laboratory work the exposure of the body to 0.012 roentgen per hour for an 8-hr day is regarded as more than the maximum dosage which should be permitted.

Extranuclear Structure. As previously pointed out, there are four fundamental experiments on which theories of atomic structure are based. The disintegration of the radioactive elements and the artificial disintegration of the light elements indicate that the nuclei of heavy atoms are composed of smaller more fundamental units. The occasional abnormal deflection of alpha particles shows that the mass of the atom must be concentrated in a nucleus occupying but a small fraction of the total atom. The mass spectrograph gives a measure of the mass of the nucleus; and the X-ray measurements of the atomic number reveal the number of excess positive charges on the nucleus, and the number of electrons surrounding the nucleus. The atomic number is of the greatest interest in chemistry, for the number and arrangement of these extranuclear electrons determines the position of an element in the periodic table and its chemical properties. A form of the periodic table arranged by Professor M. L. Holt, of the University of Wisconsin, is given in Table VII, where the atomic numbers are given together with the number of electrons in the outer extranuclear shells and subshells.

The first, second, third, and fourth electron shells are known as the K, L, M, shells. They correspond to the K, L, M, N series in the X-ray spectra discussed on pages 574–622. They stand for different

values of the first or principal quantum number n. For K, $n = 1$; for L, $n = 2$; for M, $n = 3$, etc.

The rare gases are the key elements in the periodic table for they represent the completion of a shell. The number of elements in a shell or period is limited by the quantum numbers, as described on page 576.

REFERENCES

Taylor and Glasstone, "Treatise on Physical Chemistry," D. Van Nostrand Co. New York, 1942, Chapter I.

Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, 1946, Chapters I and II.

Hoag and Korff, "Electron and Nuclear Physics," D. Van Nostrand Co., 1948.

Bethe, "Elementary Nuclear Theory," John Wiley & Sons, New York, 1948.

Pollard and Davidson, "Applied Nuclear Physics," John Wiley & Sons, New York, 1942.

Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., New York, 1940.

Gamow, "Structure of Atomic Nuclei and Nuclear Structure," Oxford University Press, New York, 1937.

Lapp and Andrews, "Nuclear Radiation Physics," Prentice Hall, New York, 1948.

PROBLEMS

1. A beam of cathode rays was deflected by a magnetic field of 4.5 emu into an arc having a radius of curvature of 15 cm. An electric field of 50.0 volts per centimeter was required to bring the path of the rays back to its original position (1 volt per centimeter $= 10^8$ emu per centimeter)

(*a*) What is the velocity of the rays?

(*b*) If $e = 1.59 \times 10^{-20}$ emu, calculate the mass of an electron.

Ans. (*a*) 1.11×10^9. (*b*) 9.7×10^{-28} g.

2. Measurements on a certain radioelement gave a constant of 1.65×10^{-6} second^{-1}.

(*a*) What is its period of half-life?

(*b*) How long will it take for 99 per cent of the element to disintegrate?

(*c*) What is the name of this radioelement?

Ans. (*a*) 4.85 days. (*b*) 32.2 days. (*c*) Radium E.

3. Calculate the weight of radium E in equilibrium with 1 g of radium D.

Ans. 5.4×10^{-4} g.

4. A hospital maintained a solution containing 0.250 g of radium as a source of radon for therapeutic purposes. The radon was pumped off under reduced pressure once a week.

(*a*) How many grams of radon were obtained each week?

(*b*) What volume would it occupy under standard conditions of temperature and pressure? *Ans.* (*a*) 1.15×10^{-6} g. (*b*) 0.116 cu mm.

5. Radioactive carbon is obtained from the Atomic Energy Commission at Oak Ridge in the form of barium carbonate. (*a*) If the carbon contains 3 per cent radioactive carbon 14, 1 per cent carbon 13, and 96 per cent carbon 12, how many grams

of the barium carbonate does it take to give one millicurie? (*b*) The radioactivity can be measured with sufficient accuracy for a given experiment if there are 100 disintegrations per minute, using the equivalent of 50 ml of carbon dioxide gas measured at standard conditions. How much can this material be diluted; that is, how many grams of ordinary carbon can be added to 1 g of carbon from the sample of radioactive barium carbonate, if the same accuracy of counting is to be maintained, that is, 100 counts per minute in a 50 ml sample of gas?

Ans. (*a*) 0.086 g. (*b*) 1.1×10^8.

6. If the products of a transmutation weigh 0.001 g more per gram atom than the reactants, what is the minimum energy which must be supplied to effect the transmutation: (*a*) expressed in kilogram-calories per gram atom; (*b*) expressed in voltage of beta rays emitted?

Ans. (*a*) 2.2×10^7 kcal/g atom. (*b*) 9.3×10^5 volts.

7. One gram of uranium 235 evolves about 20 billion calories when it undergoes fission.

(*a*) Compare this heat of fission with the heat evolved in the combustion of 1 g of carbon. Carbon has the highest heat of combustion per gram of any organic material.

(*b*) How many tons (2000 lb) of coke will it take to give as much heat on oxidation as 1 lb (454 g) of uranium 235 evolves on fission? (Coke is assumed to be pure carbon.)

(*c*) If it is assumed that one fourth of the heat of fission is converted into electricity with standard steam boilers, turbines and dynamos, how many kilowatts of electricity can be generated by the consumption of 1 lb of uranium 235 per day?

Ans. (*a*) 7840 cal/g. (*b*) 1272 tons. (*c*) 110,000 kw.

8. Thorium B is an isotope of lead and thus has nearly identical chemical and physical properties. A given quantity of thorium B was mixed with a lead salt containing 10 mg of lead, taken into solution and precipitated as the chromate. Ten cubic centimeters of the supernatant liquid, when evaporated, gave a residue which was 1/24,000 as active as the original quantity of thorium B. What is the solubility of lead chromate in moles per liter? *Ans.* 2×10^{-7} mole per liter.

---

9. (*a*) Show mathematically that the radioactivity per micromole of a short-lived radio element is greater than that of a long-lived element.

(*b*) How many grams of radium will be required to give as much radioactivity for luminous paint as 1 g of polonium?

10. One kilogram of purified uranium is sealed in a vault as an indicator of time. If a chemist of the future finds 1 mg of lead, what year A.D. will it be?

11. Actinium emanation comes in the group of rare gases, having zero valence. It loses an α particle, the product loses another α particle, and then the new radioelement loses a β particle. (*a*) To what group in the periodic table does this radioelement belong? (*b*) Describe briefly its physical and chemical properties.

12. (*a*) Some beta particles have an initial velocity of 0.3 the velocity of light. What voltage would have to be applied to electrons in order for them to be equivalent to beta rays?

(*b*) To how many beta particles per second would an electron current of 2 milliamperes correspond?

(*c*) To how many grams of radium B would this be equivalent?

13. (*a*) Radon is removed from a sample of radium with which it was in equilibrium and is allowed to decay. Starting with 100 units of radon how many will be left after 2, 4, 8, and 16 days?

(*b*) The sample of radium immediately starts regenerating radon. How many units of radon will be in equilibrium with the radium after 2, 4, 8, and 16 days?

(*c*) Plot the data of (*a*) and (*b*) against time, and draw two curves through the points.

14. The mass spectrum of a mixture of carbon dioxide and methane gave lines which corresponded to the following ratios of mass to number of charges:

6, 8, 12, 13, 14, 15, 16, 28, 32, 44

Suggest positive ions which may be responsible for each of these lines.

15. Write the equations for several different ways of producing radioactive aluminum using neutrons, deuterons, or α particles.

16. Calculate the change in mass involved in the nuclear transformation:

$$Li^7 + H^1 = 2He^4 + \text{energy}$$

(*a*) How much energy is liberated in calories per mole?

(*b*) How much energy is liberated in electron volts?

(*c*) In what form is this energy liberated?

17. A sample of radioactive manganese was measured in a counting chamber with the following results:

Time in hours	0	0.28	0.75	2.13	7.13	10.03	12.82	17.45	∞
Counts per minute	20,862	19,197	17,129	11,602	3,159	1,451	690	246	27

The continuing value of 27 counts per minute is due to background and to long-lived impurities in the manganese. Which isotope of manganese was this as identified by its half-life and atomic mass?

18. An element gives off beta rays at 1.5 million electron volts. How much less per gram atom will the new element, which is formed by the radioactive decay, weigh?

19. The atomic number of phosphorus is 15.

(*a*) How are the 15 electrons around the nucleus arranged in groups?

(*b*) Show that this distribution of electrons is in agreement with the quantum numbers and Pauli principle.

(*c*) How many electrons are there in the outermost group?

20. Explain why manganese has a variable valence and bromine ordinarily does not.

---

21. An investigation of the wave lengths of the K_α lines in the X-ray spectra of various elements gave for zinc (atomic number 30) $\lambda_{K_\alpha} = 1.445$ A and for cobalt (atomic number 27) $\lambda_{K_\alpha} = 1.798$ A. A third element showed a third-order reflection from a rock-salt crystal ($d = 8.454 \times 10^{-8}$ cm) at $\theta = 36.7°$. What was the third element?

22. A sample of radioactive sodium, with a half-life of 53,300 seconds, is injected into an animal. How many days will it take for the radioactivity to fall to one tenth of its original intensity?

23. (*a*) After how many years will 1 g of polonium decay to such a point that it is equivalent in radioactivity to 1 g of radium?

(*b*) After 10 years what will be the relative intensities of radioactivity of equal weights of radium and polonium?

24. The weight of lead in a sample of uraninite from the Black Hills of South Dakota was found to be 22.8 per cent of the weight of the uranium. Calculate from this fact a minimum age for the earth.

25. Radioactive phosphorus P^{30} can be prepared with the five different agencies, α, n, p, d, and γ rays. State what elements you would use for each process. Write the nuclear reaction in each case.

26. State what isotopic element may be produced when the following undergo radio disintegration:

$$_1H^3;\quad _6C^{11};\quad _{11}Na^{24};\quad _{35}Br^{82};\quad _{47}Ag^{108}$$

27. Calculate the change in mass and the energy involved in the nuclear transformation:

$$He^4 + N^{14} = O^{17} + H^1 + \text{energy}$$

28. How large would a proton current have to be in amperes in a high-voltage transmutation apparatus in order to correspond to one microcurie.

29. The beryllium isotope with a mass of 7.01916 emits gamma rays of 0.48 million electron volts. What is the product of this radioactive decay and what is its mass?

30. (*a*) How many grams of radioactive bromine 82 with a half-life of 34.0 hours is required in order to give a millicurie?

(*b*) How many days can one wait before the millicurie of bromine becomes worthless for an experiment which requires 100 disintegrations per minute for counting?

31. (*a*) How many kilograms of uranium 235 must be consumed per day in driving a large ship at 20 miles per hour with 100,000 kilowatts of power, if it is assumed that 25 per cent of the heat of fission can be converted into useful work through boilers, turbines, and dynamos?

(*b*) How many kilograms of uranium 235 would be consumed in traveling 20,000 miles?

---

32. On the basis of the quantum numbers and the Pauli principle place an element having 13 electrons in its proper group in the periodic table.

33. Cite all the evidence available concerning the relative stability of elements of odd and even atomic numbers.

34. Some unstable isotopes disintegrate with the emission of positrons and some with the emission of negative electrons. Considering the facts tabulated in this chapter, suggest a relation by means of which you can predict whether positrons or negative electrons will be emitted by an isotope of given mass.

35. The slow neutron flux in a certain nuclear chain-reacting pile is 10^{12} neutrons per cm^2 per second, and a 1-g sample of $MnSO_4$ is exposed to this flux in order to prepare radioactive manganese according to the reaction:

$$Mn^{55} + n^1 \rightarrow Mn^{56}$$

The Mn^{56} decays by K capture with a half-life of 2.59 hours. The $MnSO_4$ is placed in the pile for 1 hour. Assuming that the only radioactivity formed in the sample is due to Mn^{56} and taking the cross section for its formation as 12.8×10^{-24} cm^2, calculate the activity present in the sample expressed in counts per minute, 4 hours after removal from the pile. Cross section is defined as fraction of neutrons per square centimeter absorbed by an atom.

APPENDIX

This appendix includes the derivations of several equations which are mentioned in the text but not derived there. It contains also advanced material such as the Debye–Hückel theory, the detailed methods for calculating the activities of electrolytes, an introduction to the statistical thermodynamical approach, and a qualitative outline of the estimation of activation energies.

Partial Differentiation and the Gas Law

(Page 696)

The fundamental formula of partial differentiation shows that, if u is a function of both x and y, then,

$$du = \left(\frac{\partial u}{\partial x}\right)_y dx + \left(\frac{\partial u}{\partial y}\right)_x dy \tag{1}$$

If it is applied to a specific case, for example gas, it is evident that the volume v of the gas is a function of both pressure p and temperature T. Each of these variables affects the volume independently of the other. Then,

$$dv = \left(\frac{\partial v}{\partial p}\right)_T dp + \left(\frac{\partial v}{\partial T}\right)_p dT \tag{2}$$

This equation may be expressed in words as follows. The slight change in the volume of a system, produced by changing temperature and pressure simultaneously, is equal to the sum of the two quantities: (1) the change in temperature multiplied by the rate at which the volume changes with temperature alone and (2) the change in pressure multiplied by the rate at which volume changes with pressure alone.

This equation can be used to derive the simple gas law given as equation 1 on page 5 from Boyle's law and the law of Gay-Lussac and Charles. Differentiating Boyle's law,

$$v = \frac{k_1}{p} \quad (T \text{ constant})$$

yields

$$\left(\frac{\partial v}{\partial p}\right)_T = -\frac{k_1}{p^2} = -\frac{pv}{p^2} = -\frac{v}{p}$$

and differentiating the equation of Gay-Lussac and Charles,

$$v = k_2 T \quad (p \text{ constant})$$

$$\left(\frac{\partial v}{\partial T}\right)_p = k_2 = \frac{v}{T}$$

Substituting these values of $(\partial v/\partial p)_T$ and $(\partial v/\partial T)_p$ into equation 2 yields

$$dv = -\frac{v}{p}dp + \frac{v}{T}dT$$

or

$$\frac{dv}{v} + \frac{dp}{p} = \frac{dT}{T}$$

Integrating, we have

$$\ln v + \ln p = \ln T + \ln \text{constant}$$

or

$$pv = \text{constant} \times T$$

This is more generally written in the form $pv = nRT$ as given in equation 1 on page 5, where n is the number of moles of gas and R is the gas constant.

Evaluation of van der Waals' Constants a and b

(Page 15)

The three roots of van der Waals' equation become equal at the critical temperature where B, C, and D unite in a point as shown in Fig. 6. Then,

$$v^3 - \left(b + \frac{RT_c}{p_c}\right)v^2 + \frac{a}{p_c}v - \frac{ab}{p_c} = 0 \tag{1}$$

where the subscript c indicates the critical state and the three roots $v_1 = v_2 = v_3$ are all equal to v_c. Then, $v - v_c = 0$ and $(v - v_c)^3 = 0$. Expanding by the binomial theorem yields

$$(v - v_c)^3 = v^3 - 3v_c v^2 + 3v_c^2 v - v_c^3 = 0 \tag{2}$$

Equating the coefficients of v in equations 1 and 2, we have

$$3v_c^2 = \frac{a}{p_c} \tag{3}$$

and, equating the constant terms,

$$v_c^3 = \frac{ab}{p_c} \tag{4}$$

It is possible then to determine the values of the constants a and b for any gas from a knowledge of the critical volume and critical pressures, thus:

$$a = 3p_c v_c^2 \tag{5}$$

Dividing equation 4 by equation 3 gives

$$b = \frac{v_c}{3} \tag{6}$$

By equating the coefficients of v^2 in a similar manner and substituting the values of v_c and p_c it can be shown that

$$R = \frac{8}{3}\frac{p_c v_c}{T_c} \tag{7}$$

Obviously a, b, and R must be expressed in the same units as p and v.

The Beattie–Bridgman Equation of State

(Page 21)

The Beattie–Bridgman * equation is

$$p = \frac{RT}{V^2}\left[V + B_0\left(1 - \frac{b}{V}\right)\right]\left[1 - \frac{c}{VT^3}\right] - \frac{A_0}{V^2}\left(1 - \frac{a}{V}\right)$$

The five constants must be evaluated from experimental data on each gas. They are recorded in the literature for a few of the common gases. For carbon dioxide, the constants are $A_0 = 5.0065$; $B_0 = 0.10476$; $a = 0.07132$; $b = 0.07235$; $c = 6.60 \times 10^5$. The equation may be illustrated by calculating the pressure p exerted by a mole of carbon dioxide at 50.00° in a given volume.

$$p = \frac{0.08206 \times 323.15}{V^2}\left[V + 0.10476\left(1 - \frac{0.07235}{V}\right)\right]\left[1 - \frac{6.60 \times 10^5}{V(323.15)^3}\right] - \frac{5.0065}{V^2}\left(1 - \frac{0.07132}{V}\right)$$

When $V = 0.300$ liter

$$p = 294.66\ (0.300 + 0.079495)(0.9348) - 55.63\ (0.76227)$$
$$= 104.53 - 42.41 = 62.12 \text{ atm}$$

Distance between 111 Planes

(Page 50)

$$d_{111} = \frac{1}{\sqrt{3}}$$

In Fig. 15*c* or 16*c* three (111) planes are shown, and the vertical distance between any two of them is to be calculated. Proceeding from the origin (that is, the central point in the lowest central line), one finds the oblique line ending in an arrow, at right angles to the plane. This is the distance d which is sought.

If the line is continued until it hits the upper right-hand corner, it forms a diagonal of the cube. Geometrical considerations show that the diagonal of the cube will intersect the planes at right angles.

Now, the length l of the diagonal of a cube is given by the expression,

$$l^2 = x^2 + y^2 + z^2 \tag{1}$$

where x, y, and z are the three sides of the cube. But, by definition of the (111) plane,

$$x = y = z = 1 \tag{2}$$

since the plane cuts each of the three axes at a distance of unity.

Then,

$$l^2 = x^2 + y^2 + z^2 = 1^2 + 1^2 + 1^2 = 3 \tag{3}$$

By inspection of these figures it is evident that the diagonal is divided into three sections by these three parallel (111) planes. When other cubes are laid down around

* Beattie and Bridgman, *J. Am. Chem. Soc.*, **49**, 1665 (1927); **50**, 3133 (1928).

these cubes, it can be seen from the intersection on the upper faces that the (111) planes are parallel and separated by constant differences.

Then the distance d between the two planes or, in fact, between any two planes is given by the relation,

$$d = \tfrac{1}{3}l = \tfrac{1}{3}\sqrt{3} \tag{4}$$

or

$$d_{111} = \frac{1}{\sqrt{3}} \tag{5}$$

Calculation of Refractive Index from Angle of Refraction

(Page 68)

The light passes through the (Pulfrich) refractometer prism as shown in **Fig. 160.**

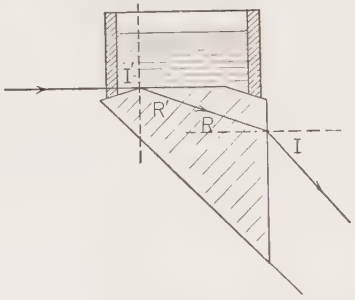


FIG. 160. Calculation of refractive index from angle of refraction.

The refractive index n at the air–liquid interface may be obtained from the refractive index N at the air–glass interface and the refractive index n_1 at the liquid–glass interface. If N is divided by n_1, the refraction in glass can be made to disappear. Therefore,

$$n = \frac{N}{n_1} = \frac{N}{\dfrac{\sin I'}{\sin R'}} \tag{1}$$

But $I' = 90°$, and $\sin I' = 1$,

$$n = \frac{N}{\dfrac{1}{\sin R'}} = N \sin R' \tag{2}$$

and, since $\sin R' = \cos R = \sqrt{1 - \sin^2 R}$

$$n = N\sqrt{1 - \sin^2 R} \tag{3}$$

For air–glass,

$$N = \frac{\sin I}{\sin R}; \quad \text{or} \quad \sin^2 R = \frac{\sin^2 I}{N^2} \tag{4}$$

and, substituting, we have

$$n = N\sqrt{1 - \frac{\sin^2 I}{N^2}} = \sqrt{N^2 - \sin^2 I} \tag{5}$$

The value of the refractive index N of the glass prism against air is supplied with the refractometer.

$C_p - C_v = R$

(Page 115)

The method of partial differentiation may be illustrated in the following proof that

$$C_p - C_v = R \tag{1}$$

This equation was developed in a different way on page 115. The molar heat capacity at constant pressure C_p is defined as the rate of change of enthalpy with temperature at constant pressure. The molar heat capacity at constant volume C_v is defined as the rate of change of internal energy E with temperature at constant volume.

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \text{and} \quad C_v = \left(\frac{\partial E}{\partial T}\right)_v \tag{2}$$

Therefore,

$$C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial E}{\partial T}\right)_v$$

$$= \left[\frac{\partial (E + pv)}{\partial T}\right]_p - \left(\frac{\partial E}{\partial T}\right)_v$$

$$= \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial E}{\partial T}\right)_v \tag{3}$$

But, since E is a single-valued function of the variables T and v, it follows that

$$dE = \left(\frac{\partial E}{\partial T}\right)_v dT + \left(\frac{\partial E}{\partial v}\right)_T dv \tag{4}$$

and differentiating with respect to T at constant pressure gives

$$\left(\frac{\partial E}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_v + \left(\frac{\partial E}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \tag{5}$$

Substituting in equation 3, we obtain

$$C_p - C_v = \left(\frac{\partial E}{\partial T}\right)_v + \left(\frac{\partial E}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial E}{\partial T}\right)_v \tag{6}$$

But for an ideal gas $(\partial E/\partial v)_T = 0$ (page 110). Hence equation 6 becomes

$$C_p - C_v = p\left(\frac{\partial v}{\partial T}\right)_p \tag{7}$$

and, since $v = RT/p$, we may replace $(\partial v/\partial T)_p$ by R/p, and equation 7 then simplifies to

$$C_p - C_v = R \tag{8}$$

The use of partial differentiation may be illustrated further in the study of the Joule–Thomson effect discussed on page 112.

Since H is a single-valued function of any two of the three variables T, p, and v, the general rule for partial differentiation may be applied; choosing temperature and pressure as the variables, we may write

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \tag{9}$$

But, in case of the free expansion of gas, H is constant and $dH = 0$, so that, on rearranging terms, we have

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{-\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = \frac{-\left(\frac{\partial H}{\partial p}\right)_T}{C_p} \tag{10}$$

Writing for H its equivalent $E + pv$, we have

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{-\left(\frac{\partial (E + pv)}{\partial p}\right)_T}{C_p} = -\frac{1}{C_p}\left(\frac{\partial E}{\partial p}\right)_T - \frac{1}{C_p}\left(\frac{\partial (pv)}{\partial p}\right)_T \tag{11}$$

In this equation $-(\partial E/\partial p)$ corresponds to the decrease in internal energy as the molecules are crowded closer together, a process which liberates heat and causes the temperature to rise if the system is thermally insulated. According to this term a *decrease* in pressure should produce a drop in the temperature.

If we neglect the term $-\frac{1}{C_p}\left(\frac{\partial E}{\partial p}\right)_T$ and consider only the last term of the equation, if pv increases when p decreases dT/dp will have a positive value, and the gas will tend to be cooled when the pressure is decreased by the passage of the gas through a porous plug. If pv decreases when p decreases $\partial(pv)/\partial p$ will be positive, and dT/dp will be negative, indicating that the temperature will rise.

The Carnot Cycle

(Page 160)

The Carnot cycle makes use of an imaginary engine operating through a reversible cycle as indicated in **Fig. 161.** One mole of an ideal gas is enclosed in a cylinder with a weightless frictionless piston and subjected to the following four successive steps.

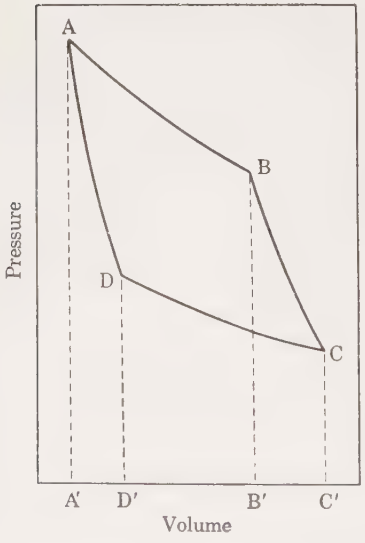


FIG. 161. Schematic pressure–volume diagram for a gas in Carnot's cycle.

1. AB represents isothermal reversible expansion from v_A to v_B at temperature T_2.

$$w_{AB} = \text{area } ABB'A' = RT_2 \ln \frac{v_B}{v_A}$$
$$q_{AB} = w_{AB} \tag{1}$$

2. BC represents adiabatic expansion from v_B to v_C. The temperature drops from T_2 to the lower temperature T_1. No heat is transferred, and the energy for doing the work must come from the cooling of the gas, ΔE.

$$q_{BC} = 0$$
$$w_{BC} = \text{area } BCC'B' = C_v(T_2 - T_1) \tag{2}$$

Also,

$$C_v \ln \frac{T_1}{T_2} = -R \ln \frac{v_C}{v_B} \quad \text{(adiabatic expansion)} \tag{3}$$

3. CD represents isothermal reversible compression from v_C to v_D at temperature T_1.

$$w_{CD} = \text{area } CC'D'D = RT_1 \ln \frac{v_D}{v_C}$$

$$w_{CD} = q_{CD} \tag{4}$$

4. DA represents adiabatic compression from v_D to v_A. The temperature rises from T_1 to T_2.

$$q_{DA} = 0$$

$$w_{DA} = \text{area } DD'A'A = C_v(T_1 - T_2) = -C_v(T_2 - T_1) \tag{5}$$

Also,

$$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{v_A}{v_D} \tag{6}$$

The gas is now at its starting point under the original conditions of temperature, pressure, and volume, and the four steps constitute a reversible cycle. Work done by the system w is given by the area, $ABCC'A'$, and work done on the system by its surroundings is given by the area, $CDAA'C'$. More work is obtained at the higher temperature than is required at the lower temperature, and the net work is represented by the area $ABCD$. To offset this surplus work a quantity of heat is transferred from a higher temperature T_2 to a lower one T_1. This work represents the maximum work obtainable because the cycle is reversible.

The total work w is as follows:

$$w = w_{AB} + w_{BC} + w_{CD} + w_{DA} = RT_2 \ln \frac{v_B}{v_A} + C_v(T_2 - T_1)$$

$$+ RT_1 \ln \frac{v_D}{v_C} + (-C_v[T_2 - T_1]) * \tag{7}$$

$$w = RT_2 \ln \frac{v_B}{v_A} + RT_1 \ln \frac{v_D}{v_C} = RT_2 \ln \frac{v_B}{v_A} - RT_1 \ln \frac{v_C}{v_D} \tag{8}$$

In order to obtain a further simplification, the last equations of steps 2 and 4 are compared:

$$\frac{C_v}{R} \ln \frac{T_1}{T_2} = -\ln \frac{v_C}{v_B} \tag{9}$$

and

$$\frac{C_v}{R} \ln \frac{T_2}{T_1} = -\ln \frac{v_A}{v_D} \tag{10}$$

or

$$\frac{C_v}{R} \ln \frac{T_1}{T_2} = -\ln \frac{v_D}{v_A} \tag{11}$$

Obviously,

$$\frac{v_C}{v_B} = \frac{v_D}{v_A} \tag{12}$$

and rearranging gives

$$\frac{v_C}{v_D} = \frac{v_B}{v_A} \tag{13}$$

* It may be noted that all the work terms are *added* and that the relative magnitudes of the final and initial states determine the sign.

Substituting equation 13 into equation 8, we have

$$w = RT_2 \ln \frac{v_B}{v_A} - RT_1 \ln \frac{v_B}{v_A} \tag{14}$$

Dividing this equation by $q_{AB} = RT_2 \ln v_B/v_A$, as given in the first step, yields

$$\frac{w}{q_{AB}} = \frac{R(T_2 - T_1) \ln \dfrac{v_B}{v_A}}{RT_2 \ln \dfrac{v_B}{v_A}} = \frac{T_2 - T_1}{T_2} \tag{15}$$

Writing q_2 instead of q_{AB} for the heat absorbed at the higher temperature T_2, and remembering that the work is maximum work because the cycle is reversible, we find

$$w_{\text{max.}} = q_2 \frac{T_2 - T_1}{T_2} \tag{16}$$

This is the same as equation 39 on page 160 derived in a more general way.

The Maxwell Distribution Law

(Page 368)

The mathematical statement * of the distribution of velocities is

$$\frac{dn}{n} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-(Mv^2/2RT)} v^2 \, dv \tag{1}$$

where M is the molecular weight, v is the probable velocity of the molecule, and dn/n is the fraction of the molecules having velocities between v and $v + dv$, n being the total number of molecules, which is a constant.

Introducing E, the energy expressed in calories per mole, we find

$$E = \tfrac{1}{2}Mv^2$$

$$dE = Mv \, dv$$

$$\frac{dn}{n} = \frac{2}{\sqrt{\pi}} \left(\frac{1}{RT}\right)^{3/2} e^{-E/RT} E^{1/2} \, dE \tag{2}$$

This gives the fraction of the molecules having energies between E and $E + dE$.

Of particular interest in physical chemistry is the number of molecules n' having energies greater than some fixed value E per mole.

Integration between E and infinity gives n_E'/n, the fraction of molecules which have energies greater than E.

$$\frac{n_E'}{n} = \int_E^\infty \frac{2}{\sqrt{\pi}} \left(\frac{1}{RT}\right)^{3/2} e^{-E/RT} E^{1/2} \, dE \tag{3}$$

$$= \frac{2}{\sqrt{\pi}} \left(\frac{E}{RT}\right)^{1/2} e^{-E/RT} \left\{1 + \frac{RT}{2E} - \left(\frac{RT}{2E}\right)^2 + \cdots\right\}$$

* A derivation is given in Glasstone "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, 1946, page 267.

In practical applications E is large compared to RT, and so the only term of importance in the brackets is the first, or

$$\frac{n_E'}{n} = \frac{2}{\sqrt{\pi}}\left(\frac{E}{RT}\right)^{1/2} e^{-E/RT} \tag{4}$$

The Rate Equation

(Page 376)

Eyring's equation for the activated complex is

$$k = \frac{RT}{Nh}\, e^{\Delta S_a/R} e^{-\Delta H_a/RT} \tag{1}$$

The concentration of the activated molecules is given in terms of an equilibrium constant K_a and the concentration of the reacting molecules, thus:

$$c_{\text{activated molecules}} = K_a c_{\text{reactants}} \sqrt{\frac{2\pi MRT}{N^2h^2}}\, l$$

$$= e^{-\Delta F_a/RT}\left(\sqrt{\frac{2\pi MRT}{N^2h^2}}\, l\right) c_{\text{reactants}} \tag{2}$$

where the term under the square-root sign allows for the fact that, in addition to the three translational degrees of freedom, there is an extra degree of freedom along which the activated molecule is decomposing. N is the Avogadro number, h is Planck's constant, and l is a measure of the width of the activated state on the energy surface. The activated molecules are moving along the top of the energy barrier with a velocity $\sqrt{RT/2\pi M}$ so that the length of time spent in the activated state is $l/\sqrt{RT/2\pi M}$. Then the rate of the reaction is given by the expression,

$$\text{Rate} = \frac{\text{number of molecules in activated state}}{\text{average time spent in activated state}} = \frac{e^{-\Delta F_a/RT}\left(\sqrt{\frac{2\pi MRT}{N^2h^2}}\, l\right) c_{\text{reactants}}}{l \div \sqrt{\frac{RT}{2\pi M}}} \tag{3}$$

$$\text{Rate} = \frac{RT}{Nh}\, e^{-\Delta F_a/RT} c_{\text{reactants}} \tag{4}$$

and

$$k = \kappa \frac{RT}{Nh}\, e^{\Delta S_a/R} e^{-\Delta H_a/RT} \tag{5}$$

The term κ is included to allow for the probability that a molecule once fully activated will give the products of the reaction. Ordinarily, it is assumed that this probability is practically unity, and κ is neglected.

Debye–Hückel Theory

(Page 512)

Surrounding any ion in a solution there will be on the average a greater number of ions of opposite charge than of like charge, as a result of the attraction of unlike charges and repulsion of like charges. For a 1 1 electrolyte, the number of positive ions dn_+ or of negative ions dn_- in a volume dV at a distance r from a particular ion will be, according to the Boltzmann distribution law,

$$dn_+ = ne^{-\epsilon\psi/kT}\,dV \tag{1}$$

$$dn_- = ne^{+\epsilon\psi/kT}\,dV \tag{2}$$

Here n is the total number of positive or negative ions divided by the total volume, k is the Boltzmann constant, and ϵ is the charge on a univalent positive ion. ψ is the electric potential or the work required to bring a unit positive charge from infinity to a distance r from the selected ion. The number of ions in the volume dV will, of course, fluctuate as the ions move about in the solution, but the equations hold for the values averaged over a period of time.

The density of charge ρ will be

$$\rho = \frac{(dn_+ - dn_-)\epsilon}{dV} = n\epsilon(e^{-\epsilon\psi/kT} - e^{\epsilon\psi/kT}) \tag{3}$$

Expanding the exponential terms into a series and neglecting higher terms, we have, as a close approximation for small potentials,

$$\rho = -\frac{2n\epsilon^2\psi}{kT} \tag{4}$$

The Poisson equation, derived from Coulomb's law, also relates ψ and ρ. Since ψ depends only on r, the equation is

$$\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} = \frac{-4\pi\rho}{D} \tag{5}$$

In this equation D is the dielectric constant of the medium. Substituting equation 4 into equation 5, we have

$$\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} = \frac{8\pi n\epsilon^2\psi}{DkT} = \kappa^2\psi \tag{6}$$

where

$$\kappa^2 = \frac{8\pi n\epsilon^2}{DkT} \tag{7}$$

It can be verified that a solution of equation 6 is given by

$$\psi = A\frac{e^{-\kappa r}}{r} + B\frac{e^{\kappa r}}{r} \tag{8}$$

and, since there are two independent arbitrary constants A and B, this must be a general solution. The potential must approach zero as the distance r from the selected ion becomes very large, and so B must be zero; otherwise the term $e^{\kappa r}/r$ will make ψ very large at large values of r.

A can be evaluated by making use of the fact that the total charge surrounding the ion (which we will assume to be positive) must be $-\epsilon$, since the solution as a whole is neutral. Comparison of equations 5 and 6 shows that

$$\rho = -\frac{D\kappa^2\psi}{4\pi} = -\frac{D\kappa^2 A e^{-\kappa r}}{4\pi r} \tag{9}$$

Hence, integrating (by parts) from the closest distance of approach of the ions, which we will call a, gives

$$\begin{aligned} -\epsilon &= \int_a^\infty 4\pi r^2 \rho \, dr \\ &= -\int_a^\infty r D\kappa^2 A e^{-\kappa r} \, dr \\ &= -DAe^{-\kappa a}(1 + \kappa a) \end{aligned} \tag{10}$$

Therefore,

$$A = \frac{\epsilon e^{\kappa a}}{D(1 + \kappa a)} \tag{11}$$

and

$$\psi = \frac{\epsilon e^{\kappa(a-r)}}{D(1 + \kappa a)r} \tag{12}$$

The potential at the ion is the value of ψ at $r = a$,

$$\psi = \frac{\epsilon}{D(1 + \kappa a)a} \tag{13}$$

In calculating the activity coefficients and other properties of the solution, Debye attributed all the deviation from the behavior of ideal solutions to the electric charges on the ions. Consider the following imaginary process.*

1. Gradually discharge an ion in an extremely dilute solution of the electrolyte.
2. Transfer the discharged ion to a more concentrated solution.
3. Gradually charge the ion again.

The changes in free energy in steps 1 and 3 are equal to the electric work done on the system, and the free-energy change in step 2 is the same as for ideal solutions.

$$\begin{aligned} \Delta F_1 &= \int_{q=\epsilon}^{q=0} \psi \, dq = \int_{q=\epsilon}^{q=0} \frac{q}{D(1 + \kappa a)a} \, dq \\ &= -\frac{\epsilon^2}{2Da} \; (\kappa \cong 0 \text{ here}) \end{aligned}$$

$$\Delta F_2 = \frac{RT}{N} \ln \frac{c}{c_0} = kT \ln \frac{c}{c_0}$$

where c and c_0 are the concentrations of the final and initial solutions, respectively.

$$\begin{aligned} \Delta F_3 &= \int_{q=0}^{q=\epsilon} \frac{q}{D(1 + \kappa a)a} \, dq = \frac{\epsilon^2}{2D(1 + \kappa a)a} \\ &= \frac{\epsilon^2}{2Da} - \frac{\epsilon^2 \kappa}{2D(1 + \kappa a)} \end{aligned}$$

* Guntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

Therefore,

$$\Delta F = \Delta F_1 + \Delta F_2 + \Delta F_3 = kT \ln \frac{c}{c_0} - \frac{\epsilon^2 \kappa}{2D(1 + \kappa a)} \tag{14}$$

The free-energy change is also given by the equation,

$$\Delta F = \frac{RT}{N} \ln \frac{\gamma c}{c_0} = kT \ln \frac{c}{c_0} + kT \ln \gamma \tag{15}$$

where γ is the activity coefficient of the ion in the final solution. $\gamma = 1$ in the initial solution.

Comparing equations 14 and 15, we see that

$$kT \ln \gamma = - \frac{\epsilon^2 \kappa}{2D(1 + \kappa a)} \tag{16}$$

If we use equation 7 and $n = c/1000N$, where c is the concentration in moles per liter and N is the Avogadro number, equation 16 may be written as

$$\log \gamma = - \frac{\epsilon^2 \sqrt{\dfrac{8\pi c \epsilon^2}{1000NDkT}}}{2.303 \times 2DkT \left(1 + a \sqrt{\dfrac{8\pi c \epsilon^2}{1000NDkT}}\right)} \tag{17}$$

If c is small, equation 17 becomes

$$\log \gamma = -A\sqrt{c} \tag{18}$$

where

$$A = \frac{\epsilon^3 (2\pi)^{1/2}}{2.303 (DkT)^{3/2} (1000N)^{1/2}} \tag{19}$$

This equation was derived for a 1 – 1 electrolyte. The expression for the activity coefficient of other types of electrolytes in solutions containing different electrolytes (page 470) can be derived in a similar manner.

For water at 25° $A = 0.503$.

Calculation of Activities of Electrolytes from Electromotive-Force Measurements

(Page 469)

The determination of activities of electrolytes by extrapolation to infinite dilution may be illustrated with hydrochloric acid.

The following cell without transference,

$$\text{Pt, } H_2 \text{ (1 atm); HCl}(m)\text{; AgCl; Ag}$$

is reversible with respect to both electrodes, and its voltage depends on the activity of hydrochloric acid. The cell reaction is

$$\tfrac{1}{2}H_2 + AgCl = H^+ + Cl^- + Ag$$

The activity coefficient of the hydrochloric acid is represented by γ, and at each concentration the activity of the hydrogen ion is γm and that of the chloride ion is also γm, where m is the molality.

The electromotive force of the cell is given by the equation (page 451):

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{H^+} \times a_{Cl^-} \times a_{Ag}}{a_{AgCl} a_{H_2}^{1/2}} = E^0 - \frac{RT}{F} \ln \gamma^2 m^2 \qquad (1)$$

where E is the measured potential and E^0 is the standard potential, that is, the electromotive force of the cell when the activity of hydrochloric acid is unity. Rearranging and putting in numerical values for 25° gives

$$E + 0.1183 \log m = E^0 - 0.1183 \log \gamma \qquad (2)$$

Since at infinite dilution $\gamma = 1$ and $\log \gamma = 0$, it can be seen that, when $E + 0.1183 \log m$ is plotted against m, the extrapolation of $E + 0.1183 \log m$ to $m = 0$ will give E^0.

In order to make a satisfactory extrapolation, use is made of the Debye–Hückel theory to furnish a function which will give nearly a straight line. From this theory is obtained the following expression for the activity coefficient of any 1–1 electrolyte (for example, HCl) in dilute aqueous solutions at 25°,

$$\log \gamma = -0.509 \sqrt{m} + bm \qquad (3)$$

where b is an empirical constant depending partly on the radii of the ions (page 513).

Substituting in equation 2 and rearranging terms yields

$$E + 0.1183 \log m - 0.0602 \sqrt{m} = E^0 - (0.1183b)m \qquad (4)$$

According to this equation, the left-hand side, which we will designate as E', will give a straight line when it is plotted against m, and its value at infinite dilution is E^0. Actually, the line will be somewhat curved, since equation 3 is exact only in very dilute solutions, but the extrapolation of E' can usually be made without difficulty.

In Table I are given the measured electromotive forces and values of E' at various molalities, and, in **Fig. 162,** E' is plotted against m. The extrapolated value is

TABLE I

ELECTROMOTIVE FORCE OF CONCENTRATION CELLS OF HCl [1]

m	E	E'
0.003564	0.51527	0.22207
0.004488	0.50384	0.22204
0.006239	0.48747	0.22188
0.008636	0.47135	0.22162
0.011195	0.45861	0.22144
0.01710	0.43783	0.22092
0.02563	0.41824	0.22036
0.05391	0.38222	0.21820

[1] Harned and Ehlers, *J. Am. Chem. Soc.*, **54,** 1350 (1932).

0.2224 volt. This is the electromotive force of the cell when hydrochloric acid is at unit activity (that is, is in its standard state), and it is also the negative of the silver–silver chloride standard electrode potential. Similar methods have been used for calculating other standard electrode potentials.

The value of E^0 having been determined, the activity coefficient of hydrochloric acid is obtained from the electromotive force of the cell for any concentration of HCl.

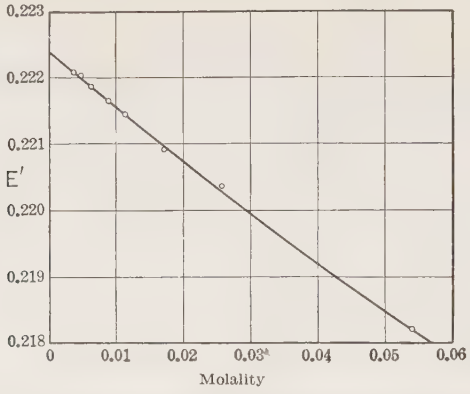


FIG. 162. A function of electromotive force measurements extrapolated to infinite dilution for determining the activity coefficients of hydrochloric acid.

For example, if the electromotive force of the cell on page 682 is 0.3524 volt for $m = 0.1$, γ may be calculated for $0.1m$ HCl (at 25°) as follows:

$$0.3524 = 0.2224 - 2 \times 0.05915 \times \log (0.1\gamma)$$

$$= 0.2224 - 0.1183 \log 0.1 - 0.1183 \log \gamma$$

$$\log \gamma = (0.2224 - 0.3524 + 0.1183)/0.1183 = -0.0989$$

$$\gamma = 0.796$$

Calculation of Activities of the Solvent from the Activities of the Solute

In a binary mixture $N_1 + N_2 = 1$, where N_1 refers to the mole fraction of the solvent and N_2 refers to the mole fraction of the solute,

$$dN_1 = -dN_2 \tag{1}$$

but since $d \ln N = dN/N$

$$N_1 \, d \ln N_1 = -N_2 \, d \ln N_2 \tag{2}$$

Furthermore, it can be shown that, for changes in concentration in binary mixtures at constant temperature and pressure, the free energy F (or any additive property) is governed by the equation, $N_1 \, dF_1 + N_2 \, dF_2 = 0$. Rearranging, we have

$$dF_1 = -\frac{N_2}{N_1} dF_2 \tag{3}$$

Substituting in this equation $RT \, d \ln a$ for dF as given on page 277 gives

$$d \ln a_1 = -\frac{N_2}{N_1} d \ln a_2 \tag{4}$$

Subtracting equation 2 from equation 4, we have

$$d \ln \frac{a_1}{N_1} = -\frac{N_2}{N_1} d \ln \frac{a_2}{N_2} \tag{5}$$

At infinite dilution the solution is essentially the same as the solvent, and then the activity a_1^0 of the solvent is practically the same as the mole fraction N_1. Then,

$$\frac{a_1^0}{N_1^0} = 1 \quad \text{and} \quad \log \frac{a_1^0}{N_1^0} = 0$$

and integrating equation (5) between infinite dilution and some specified mole fraction gives

$$\log \frac{a_1}{N_1} = -\int_0^{N_2} \frac{N_2}{N_1} d \log \frac{a_2}{N_2} \tag{6}$$

Now the integral on the right-hand side of the equation may be determined if the relation is known between N_2/N_1 and $\log a_2/N_2$; or it may be evaluated graphically by plotting N_2/N_1 against $\log a_2/N_2$ and finding the area under the curve.

This method * can be used to determine the activities of mercury in a thallium amalgam at 20° from a knowledge of the activities of thallium as illustrated in **Fig. 163.** The activities of thallium in mercury solutions were readily obtained by

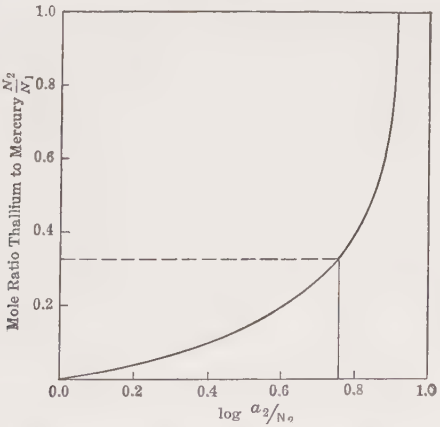


FIG. 163. Graphical method for determining the activities of the solvent from those of the solute.

measuring the potential difference between two amalgams of different concentration in contact with a solution of thallous sulfate. The measurements were carried to low concentrations, and then the value of E^0 was determined by extrapolation in a manner similar to that described for hydrochloric acid. In Table I the activities of thallium obtained in this way, at various mole fractions, are divided by the mole fractions and shown in the fourth column.

* Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 233 (1921); "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, page 269.

TABLE I

ACTIVITIES OF MERCURY IN THALLIUM AMALGAMS

Mole Fraction Thallium N_2	Mole Fraction Mercury N_1	Mole Ratio N_2/N_1	Activity Tl	Activity Hg	Activity Hg a_1
			Mole Fract. Tl a_2/N_2	Mole Fract. Hg a_1/N_1	
0	1	0	1	1	1
0.005	0.995	0.00502	1.06	0.9998	0.995
0.01	0.99	0.0101	1.15	0.999	0.989
0.05	0.95	0.0526	1.80	0.986	0.937
0.1	0.90	0.111	2.84	0.950	0.855
0.2	0.80	0.250	4.98	0.866	0.693
0.3	....	.....	6.60	.....	y
0.4	0.60	0.666	7.57	0.734	0.440
0.5	0.50	1.000	7.98	0.704	0.352

In Fig. 163 a dotted line is shown corresponding to a mole fraction of thallium of $\frac{1}{4}$ (mole ratio of $\frac{1}{3}$), and the activity of the mercury at this concentration is readily obtained after measuring the area under the curve out to the intersection with this dotted line. This area, $\int_0^{0.25} \frac{N_2}{N_1} d \log \frac{a_2}{N_2}$, is equal to $-\log a_1/N_1$, from which a_1/N_1 and a_1 may be calculated readily. The data of the last two columns were obtained by this method, carrying out the graphical integration to different limits.

A similar method can be used for calculating the activity of the solute from that of the solvent, but here the curve approaches the axis asymptotically, and the determination of the area is inaccurate. It is more satisfactory, then, to plot some arbitrary function of the activity of the solvent which approaches zero at infinite dilution. Such a method is particularly valuable in aqueous solutions where the activity of the solvent may be determined easily.

Calculation of Activities from Freezing Points

The activity of water is diminished by the addition of a solute, and this lessening of the escaping tendency leads to a lowering of the freezing point. Since freezing-point depressions can be measured more accurately than the other colligative properties of solutions, they are often used for determining the activities of the solvent, and, with an equation similar to equation 6 on page 685, they are used for determining the activities of the solute. Earlier in the book (page 237) it was shown that the concentration of a solute can be calculated approximately in a dilute solution when the freezing point of the solution and that of the solvent are known; but in calculating activities with precision it is necessary to know the freezing points not only of solutions of the specified concentrations but also of several additional concentrations out to extreme dilutions. The following equations can be obtained from

earlier pages, and with the proper substitutions it is possible to obtain a working equation from which activity coefficients can be obtained from molalities partly by graphical integrations. Application of the Clapeyron equation (page 174) to the vapor pressure of ice p_s and of pure supercooled water p_l at the same temperature gives

$$\frac{d \ln \frac{p_s}{p_l}}{dT} = \frac{\Delta H_s - \Delta H_v}{RT^2} = \frac{\Delta H_f}{RT^2} \tag{1}$$

where the ΔH values are the heats of sublimation, vaporization, and fusion, respectively. Strictly speaking, fugacities rather than pressures should be used, but the pressures are low enough to be nearly equal to the fugacities.

At the freezing point of the solution the vapor pressure p_l of the solution equals p_s. If pure liquid water is chosen as the standard state at any temperature, so that the activity of water in the solution is $a_1 = p_1/p_l$, the following equation results:

$$\frac{d \ln a_1}{dT} = \frac{d \ln \frac{p_1}{p_l}}{dT} = \frac{d \ln \frac{p_s}{p_l}}{dT} = \frac{\Delta H_f}{RT^2} \tag{2}$$

Assuming that ΔH_f is constant and integrating between the limits T, the freezing point of the solution, and T_0, the freezing point of pure water, where $a_1 = 1$, we have

$$\ln a_1 = \frac{-\Delta H_f}{R} \frac{(T_0 - T)}{TT_0} \cong \frac{-\Delta H_f}{RT_0^2} \Delta T_f \tag{3}$$

the last term being a good approximation when ΔT_f or $T_0 - T$ is small. This equation relates the activity of water in a solution to the freezing-point depression. It gives the activity at the freezing point of the solution, but the activities in a solution of given concentration are so nearly independent of temperature if the solution is dilute that a_1 can be considered as the activity of water in the solution at a specified temperature, say, 25°.

When the concentration is changed at constant temperature and pressure,

$$d \ln a_1 = \frac{-N_2}{N_1} d \ln a_2 \tag{4}$$

where a_2 is the activity of N_1 the solute.

The corresponding change in ΔT_f will be given by differentiation of equation 3:

$$d \ln a_1 = \frac{-\Delta H_f}{RT_0^2} d(\Delta T_f) \tag{5}$$

The activity a_2 of an electrolyte of type A_xB_y is related to the activity coefficient γ and molality m by

$$a_2 = (\gamma \times xm)^x(\gamma \times ym)^y = (\gamma m)^\nu x^x y^y \tag{6}$$

where $\nu = x + y$ is the number of ions per molecule. Thus, for $BaCl_2$,

$$a_2 = (\gamma m)(\gamma \times 2m)^2 = (\gamma m)^3 \times 4$$

Taking logarithms in equation 6 and differentiating gives

$$d \ln a_2 = \nu \, d \ln \gamma + \nu \, d \ln m \tag{7}$$

and combining equations 4, 5, and 7 yields

$$\nu\, d \ln \gamma + \nu\, d \ln m = \frac{N_1}{N_2} \frac{\Delta H_f}{RT_0^2} d(\Delta T_f) = \frac{d\, \Delta T_f}{1.858m} \tag{8}$$

Numerical values for water are used to give $1.858m$ in the last term.

Graphical integration of a plot of $1/1.858m$ against ΔT_f can be used to evaluate relative values of γ with the aid of this equation, but, since $1/m$ becomes infinite at $m = 0$, the equation is not convenient for extrapolation to infinite dilution. To avoid this difficulty, the j function is introduced as follows:

$$j = 1 - \frac{\Delta T_f}{1.858\nu m} \tag{9}$$

Since $\Delta T_f/m$ approaches 1.858ν in dilute solution, j approaches zero for $m = 0$.

Differentiating gives

$$dj = \frac{-d\, \Delta T_f}{1.858\nu m} + \frac{\Delta T_f\, dm}{1.858\nu m^2} \tag{10}$$

$$= \frac{-d\, \Delta T_f}{1.858\nu m} + (1 - j) \frac{dm}{m}$$

Substituting for $d\, \Delta T_f/1.858m$ in equation 8 and rearranging gives

$$d \ln \gamma = -dj - j \frac{dm}{m} \tag{11}$$

Integrating between concentrations 0 and m, we get the final working equation,

$$\ln \gamma = -j - \int_0^m j \frac{dm}{m} \tag{12}$$

where γ is the activity coefficient at the molality m. The last quantity in this equation can be obtained by graphical integration of a plot of j/m against m.

In accurate work corrections can be made for the approximations made in this treatment, such as the change in ΔH and a_1 with temperature.

Further material on the determination of activities from freezing-point measurements may be found in the literature.*

Specific Diffusion Rate

(Page 531)

The formula for the diffusion rate of a colloid particle is

$$D = \frac{RT}{N} \frac{1}{f}$$

where f is the frictional force opposing particles which move with a velocity of 1 cm per second, and D is the specific diffusion reaction rate.

* Randall and Vanselow, *J. Am. Chem. Soc.*, **46**, 2418 (1924); Scatchard, *J. Am. Chem. Soc.*, **47**, 648 (1925); Scatchard and Benedict, *J. Am. Chem. Soc.*, **58**, 837 (1936); Getman, *J. Phys. Chem.*, **34**, 1454 (1930); Robertson and LaMer, *J. Phys. Chem.*, **35**, 1953 (1931); Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1943.

The velocity v of motion of a molecule under the influence of a force K is

$$v = \frac{K}{f} \tag{1}$$

where f is the frictional resistance to the motion. If the concentration of the solution before a plane across which diffusion is taking place is c gram molecules per unit volume, cN molecules will be involved, with force K acting upon them, and

$$v = \frac{1}{cN}\frac{K}{f} \tag{2}$$

In diffusion the force acting is equal to the osmotic pressure gradient, therefore

$$K = -\frac{dP}{dx} = -RT\frac{dc}{dx} \tag{3}$$

and, by substitution and rearrangement,

$$-\frac{vc}{\frac{dc}{dx}} = +\frac{RT}{N} \times \frac{1}{f} \tag{4}$$

But the diffusion constant D is, by definition, the amount of solute which will diffuse in unit time, across unit area, under unit gradient of concentration; therefore,

$$-D\frac{dc}{dx} = vc \tag{5}$$

It follows immediately that

$$D = \frac{RT}{N} \times \frac{1}{f} \tag{6}$$

Bohr's Formula for the Energy of an Electron in an Elliptical Orbit

(Page 570)

$$E_n = -\frac{2\pi^2 m(Ze)^2 e^2}{n^2 h^2}$$

It is assumed that a negative electron moves in a circular orbit around a central nucleus which has a positive charge Ze, where Z is the atomic number and e is the unit electric charge, that is, the charge of an electron or proton.

The centrifugal force of the electron moving in its orbit is mv^2/r, where m is the mass of the electron, v is the velocity, and r is the radius of the orbit, that is, the distance between the electron and the nucleus.

The electric force of attraction is $(Ze)e/r^2$, as given by Coulomb's law.

In the stable orbit the centrifugal force must be equal and opposite to the electric force in order to maintain equilibrium.

Then,

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \tag{1}$$

The total energy E is equal to the sum of the kinetic energy E_k and the potential energy E_p.

$$E_k = \frac{1}{2}mv^2 = \frac{1}{2}\frac{Ze^2}{r} \tag{2}$$

and

$$E_p = \int_{\infty}^{r} \frac{Ze^2}{r^2}\,dr = -\frac{Ze^2}{r} \tag{3}$$

Then,

$$E = E_k + E_p = \frac{1}{2}\frac{Ze^2}{r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r} \tag{4}$$

The energy has a negative sign because the reference state with zero energy is taken as that state in which the electron is at infinite distance from the nucleus, and the lower limit of integration is taken as $r = \infty$.

These considerations apply to any coulombic field and can be applied to elliptical orbits as well as to circular orbits.

The angular momentum p of the moving electron is given by the expression,

$$p = mvr \tag{5}$$

Then substituting equations 5 and 1 into equation 4 yields

$$E = -\frac{Ze^2}{2r} = -\frac{Ze^2mv}{2p} = -\frac{Ze^2}{2p}\frac{Ze^2}{rv} = -\frac{Ze^2}{2p}\frac{Ze^2m}{p} = -\frac{mZ^2e^4}{2p^2} \tag{6}$$

If this formula were strictly correct, E would change continuously over a wide range, and a continuous spectrum containing all wave lengths would be produced. To account for the discontinuous spectrum which is actually produced, Bohr assumed that the angular momentum of the electron in its orbit must be an integral multiple of $h/2\pi$, where h is Planck's universal constant. In other words, he assumed that the only values of p which are permitted by the restrictions of the quantum theory are those which meet the requirement of the equation,

$$2\pi p = nh \quad \text{or} \quad p = \frac{nh}{2\pi} \tag{7}$$

where n is an integer 1, 2, 3, 4, etc.

Substituting into equation 6 gives

$$E_n = -\frac{mZ^2e^4(2\pi)^2}{2(nh)^2} = -\frac{2\pi^2mZ^2e^4}{n^2h^2} \tag{8}$$

Statistical Thermodynamics *

Gibbs, Boltzmann, and others applied the method of statistical mechanics to the calculation of specific heats and other thermodynamic quantities, but the calculations did not agree with the experimental values. As explained earlier in this book, it was necessary to wait for the development of the quantum theory before correct calculations could be made. It is now possible to calculate thermodynamic functions E, S,

* Eyring and Walter, *J. Chem. Education*, **18**, 73 (1941); Wilson, *Chem. Rev.*, **27**, 17 (1940).

A, F, C_p, and C_v for many simple molecules more accurately than they can be determined by direct experimental measurements. The treatment of more complicated molecules is still rather approximate, but important progress is being made.*

The general principles involved in the application of statistical mechanics to physical-chemical problems may be illustrated with the help of a simplified hypothetical system consisting of molecules in the energy state A and molecules in the energy state B, which are in equilibrium with each other; thus:

$$A \rightleftharpoons B$$

Then $\Delta F = -RT \ln K = -RT \ln (n_B/n_A)$ where n_A and n_B are the numbers of molecules in the two states under these equilibrium conditions. For the sake of simplicity, it may be assumed that the energy in the A state is effectively zero, that is, it is in the ground state.

Writing in the exponential form and remembering that $\Delta F = \Delta H - T\Delta S$, we have

$$\frac{n_B}{n_A} = e^{-\Delta F/RT} = e^{\Delta S/R} e^{-\Delta H/RT} \tag{1}$$

For this simple hypothetical system, it is assumed that there are no energy levels other than those found in the states A and B, and so there is no way in which heat can be taken up by raising the temperature, and the heat capacities and entropies of the separate molecules in the A state and B state are equal to zero. However, there may be several different states in which all the molecules have the same energy level. Such a system is said to be degenerate, and the degeneracy g is defined as the number of different states: 1, 2, 3, etc., which have the same energy content. Now these molecules of different configuration but equal energy content are uniformly mixed together in what may be considered as an ideal solution, and an "entropy of mixing" ΔS_m is involved, which is given by the expression:

$$\Delta S = R \ln g$$

which is derived as follows:

It was shown on page 245 that the free energy of transferring a substance from the pure state to an ideal solution is given by the expression,

$$\Delta F = RT \ln N$$

where N is the mole fraction in solution. When several different substances comprise the solution,

$$\Delta F = RTN_1 \ln N_1 + RTN_2 \ln N_2 + RTN_3 \ln N_3 + \cdots$$

but $\Delta S = (\Delta H - \Delta F)/T$; and, for ideal solutions, $\Delta H = 0$.

Then, $\Delta S = -R(N_1 \ln N_1 + N_2 \ln N_2 + N_3 \ln N_3 + \cdots)$.

In this system $N_1 = N_2 = N_3$, since it is assumed that all energy states are equally probable.

Then $\Delta S = -RgN_1 \ln N_1$, and, since

$$gN_1 = 1 \quad \text{and} \quad \frac{1}{N_1} = g$$

$$\Delta S = R \ln g \tag{2}$$

* Pitzer, *Chem. Rev.*, **27**, 39 (1940); Wenner, "Thermochemical Calculations," McGraw-Hill Book Co., New York, 1941, Chapters VII and VIII.

Substituting the value for entropy change ΔS in going from the A state to the B state, we have

$$e^{\Delta S/R} = e^{(R\ln g_B - R\ln g_A)/R} = \frac{g_B}{g_A}$$

Then

$$\frac{n_B}{n_A} = \frac{g_B}{g_A} e^{-\Delta H/RT} \tag{3}$$

where ΔH is the heat absorbed in going from the B state to the A state. Then, substituting molecular quantities for molar quantities gives

$$\frac{n_B}{n_A} = \frac{g_B}{g_A} e^{-\epsilon_B/kT}$$

where ϵ_B/kT is obtained from $\Delta H/RT$ by dividing through by Avogadro's number.

It is evident that, if a third state C were specified, the same formula would apply with subscript C taking the place of subscript B. In general,

$$\frac{n_i}{n_0} = \frac{g_i}{g_0} e^{-\epsilon_i/kT} \tag{4}$$

where n_0 and g_0 emphasize that the first state is the ground state and i represents any state. The number g_i gives the a priori probability or the statistical weight of the energy state i.

These equations are known as the Maxwell–Boltzmann equations which constitute a theoretical foundation for many of the formulas which have been discussed in earlier chapters dealing with the influence of temperature on chemical equilibrium, solubility, vapor pressure, reaction rates, and so on. They can be derived also by statistical mechanics without the use of physical-chemical formulas. According to one method a system of harmonic oscillators is used as the starting point.

Rearranging equation 4 gives

$$n_i = \left(\frac{n_0}{g_0}\right) g_i e^{-\epsilon_i/kT}$$

The sum of the numbers of molecules in all the states must equal the total number of molecules; hence, for a system of N molecules,

$$N = \Sigma_i n_i = \left(\frac{n_0}{g_0}\right) \Sigma_i g_i e^{-\epsilon_i/kT}$$

Now the total energy of the N molecules in excess of the energy in the ground state (approximately at absolute zero) is given by the expression,

$$E^0 - E_0{}^0 = \Sigma_i \epsilon_i n_i = \left(\frac{n_0}{g_0}\right) \Sigma_i \epsilon_i g_i e^{-\epsilon_i/kT}$$

$$= N \left(\frac{\Sigma_i \epsilon_i g_i e^{-\epsilon_i/kT}}{\Sigma_i g_i e^{-\epsilon_i/kT}}\right) \tag{5}$$

where $E_0{}^0$ is the energy of formation per mole of the molecules from gaseous atoms at absolute zero. These formulas may be written more simply if we use a function known as the *partition function*, defined as

$$Q = \Sigma_i g_i e^{-\epsilon_i/kT}$$

Then, it follows that

$$n_i = \frac{N}{Q} g_i e^{-\epsilon_i/kT} \tag{6}$$

and

$$\frac{-(E^0 - E_0{}^0)}{T} = \left(\frac{N}{Q}\right) \Sigma_i g_i \epsilon_i e^{-\epsilon/kT}$$

$$= \left(\frac{N}{Q}\right) kT^2 \frac{dQ}{dT} = RT^2 \frac{d \ln Q}{dT} \tag{7}$$

Similar analytical expressions may be obtained:

$$C_v = \frac{dE}{dT} = -R \frac{d}{dT}\left(\frac{d \ln Q}{d \frac{1}{T}}\right) \tag{8}$$

$$S = R\left(\ln Q + T \frac{d \ln Q}{dT}\right) \tag{9}$$

$$\frac{-(F - E^0)}{T} = R(\ln Q - 1) \tag{10}$$

These formulas giving the thermodynamic quantities in terms of the function Q are of value because of the fact that analytic expressions can usually be found for Q which avoid the necessity of tedious summations. Spectroscopic evidence indicates that we may usually break up the energy of a given level ϵ_i into separate parts (page 595), writing

$$\epsilon_i = \epsilon_{tr} + \epsilon_{el} + \epsilon_v + \epsilon_r \tag{11}$$

where these components are the translational, electronic, vibrational, and rotational energies, respectively. From the exponential nature of the partition function, it follows that we may write Q as a product of corresponding component partition functions:

$$Q = Q_{tr} \times Q_{el} \times Q_v \times Q_r \tag{12}$$

The thermodynamic functions themselves involve the logarithm of the partition function and may, therefore, be broken up into sums; for example, the entropy may be written

$$S = S_{tr} + S_{el} + S_v + S_r \tag{13}$$

It is found that in almost all cases the electronic-energy levels lie so high that only a negligible fraction of the molecules are electronically excited by thermal agitation, and, hence, the electronic contributions may usually be ignored. The vibrational contributions are evaluated by summation. The translational and rotational contributions may be closely approximated, at ordinary temperatures, by analytic functions of the molecular weight, and by moments of inertia of the molecule.

Tables are now available giving values of $-(F^0 - E_0{}^0)/T$ at various temperatures for many of the hydrocarbons and simple molecules.*

* Pitzer, *Chem. Rev.*, **27,** 39 (1940); Wilson, *Chem. Rev.*, **27,** 17 (1940); Wenner, "Thermochemical Calculations," McGraw-Hill Book Co., New York, 1941; Johnston and Davis, *J. Am. Chem. Soc.*, **56,** 271 (1934); Rossini and associates, "Physical Chemical Properties of Pure Hydrocarbons," National Bureau of Standards and American Petroleum Institute, Washington, D. C., 1947; Hougen and Watson, "Chemical Process Principles," John Wiley & Sons, New York, 1947.

Using these values together with one experimental value in order to calculate ΔE_0^0, one can calculate ΔF^0 and, thus, the chemical equilibrium constant, using the relation $-\Delta F^0 = RT \ln K$.

Calculation of Activation Energies

It is to be hoped that theoretical chemistry will provide a means of calculating from a few fundamental constants not only the thermodynamical quantities and equilibrium constants (pages 286–690) but energies of activation and reaction rates as well. A beginning has been made. However, so many more variables are involved, such as time, catalysts, foreign materials, and light, that the developments will be much slower, and the results will be subject to much greater errors. Moreover, in thermodynamics one can handle and measure the substances involved, but in chemical kinetics many of the most important substances have only a fleeting existence and cannot be investigated by direct methods. However, from a practical standpoint the prediction of reaction rates is so important that even approximate results are welcome.

The importance of the activation energy and its use in calculating reaction rates with the formula,

$$k = se^{-\Delta H_a/RT} \tag{1}$$

were stressed in Chapter XIV. If one could place all the atoms involved in a given reaction at all different positions in space and determine the energy of the system at all these different spacings he would then know the most stable products and the energies required to bring up the reactants into such positions that the given products would result. The problem is complicated because every atom interacts with every other atom and because, as already explained, there are both electrostatic and quantum mechanical attractions.

The problem has been attacked by Eyring.* It is *assumed* that the atom pairs retain their individuality until they reach such a configuration that the atoms can either return to give the original molecule or rearrange to give the new products. The general plan is to build up curves giving energies as a function of distance for all the different atom pairs and arrange them in three dimensions with energies plotted vertically from a basal plane. Theoretically, these curves can be built up from quantum numbers and spectroscopic constants when these are known sufficiently well. In the absence of these more complete data, Morse curves are used, as described on page 588, and in calculating them it is necessary to know three things: the vibration frequencies of the atoms, the interatomic distances in the normal molecule, and the heats of dissociation. These constants are now available for several atom pairs.

Energy contours are built up by solving the complicated equations which allow for the mutual interactions between all the atoms, and the object is to find the least amount of energy which can be supplied to push the atoms from their stable positions in the reactants to their stable positions in the products. In other words, the lowest mountain pass separating two valleys in an energy contour map is sought, and the height of this pass is the energy of activation.

Such an energy contour map is shown in **Fig. 164** for the addition of bromine to the double bond of an unsaturated organic compound. The two bromine atoms in the stable bromine molecule rest in energy valleys running vertically on the page. As

* Eyring, *Chem. Rev.*, **10**, 103 (1932); Glasstone, Laidler, and Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, 1941.

they come close to the carbon–carbon double bond, the old forces of attraction are altered, and the new ones are formed. After going over an energy hill at the lowest possible point, they settle down into low-energy valleys again in a stable carbon–bromine compound. The routine calculations are reduced because the only object is to find the minimum energy required, and rough estimates are adequate

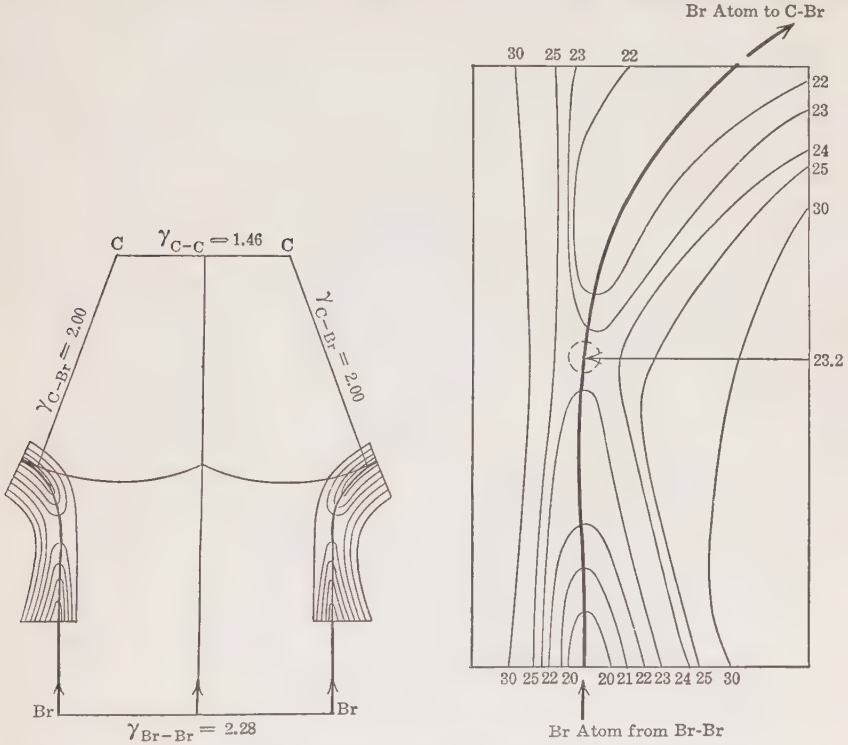


Fig. 164. Energy contour map for the addition of bromine to the carbon double bond.

for most of the map; special care and frequent calculations are necessary only in the region of the pass separating the two valleys. An enlarged scale of this region is shown at the right in Fig. 164. The approximations necessary to give practical solutions for calculating these energy contours are so great that the method is not yet satisfactory.

Mathematical Formulas *

Calculus

Δ = small finite increment; d = differential; dy/dx = derivative = limit of $\Delta y/\Delta x$ as Δx approaches zero

$y = x^n$; $dy/dx = nx^{n-1}$

$y = f_1(x) + f_2(x)$; $dy/dx = \dfrac{df_1(x)}{dx} + \dfrac{df_2(x)}{dx}$

$y = k$; $dy/dx = 0$

$y = kf(x)$; $dy/dx = k\dfrac{df(x)}{dx}$

$y = uw$; $dy/dx = u\,dv/dx + v\,du/dx$

$y = u/v$; $dy/dx = \dfrac{v\,du/dx - u\,dv/dx}{v^2}$

$y = e^x$; $dy/dx = e^x$

$y = \log_e x$; $dy/dx = 1/x$

$y = \log x$; $dy/dx = 0.4343/x$

$y = \log_a x$; $dy/dx = \dfrac{\log_a e}{x}$

$y = a^x$; $dy/dx = a^x \log_e a$

$y = f_2[f_1(x)] \cdot dy/dx = \dfrac{df_2[f_1(x)]}{d[f_1(x)]} \times \dfrac{d[f_1(x)]}{dx}$

For a maximum or minimum or point of horizontal inflection, $dy/dx = 0$.

For a differential, $dy = (dy/dx)\,dx$.

For partial differentiation where $u = f(x, y, z)$,

$$du = \left(\frac{\partial u}{\partial x}\right)_{y,z} dx + \left(\frac{\partial u}{\partial y}\right)_{x,z} dy + \left(\frac{\partial u}{\partial z}\right)_{x,y} dz$$

$$\int dx = x + C$$

$$\int x^n\,dx = x^{n+1}/(n+1) + C$$

$$\int x^{-1}\,dx = \log_e x + C$$

$$\int kf(x)\,dx = k\int f(x)\,dx$$

$$\int [f_1(x) + f_2(x) + f_3(x)]\,dx = \int f_1(x)\,dx + \int f_2(x)\,dx + \int f_3(x)\,dx$$

$$\int [k + f(x)]\,dx = \int k\,dx + \int f(x)\,dx = kx + \int f(x)\,dx + C$$

$$\int e^x\,dx = e^x + C$$

* An elementary treatment of the mathematics needed for the study of physical chemistry is given by Daniels, "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., New York, 1928.

$$\int a^x\,dx = \frac{a^x}{\log_e a} + C$$

$$\int \log_e x\,dx = x(\log_e x - 1) + C$$

$$\int \log x\,dx = 0.4343x(\log x - 1) + C$$

$$\int \log_a x\,dx = (\log_a e)(x)(\log_e x - 1) + C$$

Integrating between limits gives $\int_a^b x\,dx = \left[\frac{x^2}{2}\right]_a^b = \frac{b^2}{2} - \frac{a^2}{2}$

Trigonometry

sine = ordinate/hypotenuse
cosine = abscissa/hypotenuse
tangent = ordinate/abscissa
$1^\circ = 0.0175$ radian
$\sin^2 x + \cos^2 x = 1$
$y = \sin x;\ dy/dx = \cos x$
$y = \cos x;\ dy/dx = -\sin x$
$y = \tan x;\ dy/dx = \sec^2 x$

$$\int \sin x\,dx = -\cos x + C$$

$$\int \cos x\,dx = \sin x + C$$

Miscellaneous

If $ax^2 + bx + c = 0$, $\quad x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

1 inch = 2.54 cm 1 pound = 453.6 g
log means $\log_{10}$; ln means $\log_e$

Greek Alphabet

A	α	Alpha	N	ν	Nu
B	β	Beta	Ξ	ξ	Xi
Γ	γ	Gamma	O	o	Omicron
Δ	δ	Delta	Π	π	Pi
E	ϵ	Epsilon	P	ρ	Rho
Z	ζ	Zeta	Σ	σ	Sigma
H	η	Eta	T	τ	Tau
Θ	θ	Theta	Υ	υ	Upsilon
I	ι	Iota	Φ	ϕ	Phi
K	κ	Kappa	X	χ	Chi
Λ	λ	Lambda	Ψ	ψ	Psi
M	μ	Mu	Ω	ω	Omega

Symbols Used for the More Common Abbreviations

A	work content
A	angstrom unit
C	molar heat capacity
E	internal energy; activation energy
$\boldsymbol{E}$	voltage
emf	electromotive force
F	free energy
ΔF	change in free energy
ΔF^0	change in free energy (standard state)
$\boldsymbol{F}$	faraday (96,496 coulombs)
H	enthalpy
I	intensity of light
K	equilibrium constant; absolute temperature scale
K_b	boiling-point constant
K_f	freezing-point constant
L	specific conductance
M	molecular weight; molarity
N	Avogadro number; mole fraction
P	osmotic pressure
R	gas constant
$\boldsymbol{R}$	Rydberg constant
S	entropy
T	absolute temperature
V	volume of 1 mole of gas
$\overline{V}$	partial molal volume
a	activity
c	concentration; heat capacity
d	density
e	electron; electronic charge
h	Planck's constant
k	specific reaction rate; gas constant per molecule
m	molality
n	number of moles; refractive index
p	pressure
pH	measure of hydrogen-ion activity; $-\log a_{H^+}$
q	heat absorbed
t	centigrade temperature; time
v	volume
w	work done
α	angle of optical rotation
γ	activity coefficient; surface tension
ϵ	quantum
η	viscosity
Λ	equivalent conductance
λ	wave length of radiation
μ	micron; dipole moment
ν	frequency of radiation
$\tilde{\nu}$	wave number
Φ	quantum yield

Table of Physical-Chemical Constants

These constants have been calculated on the basis of the adoption of the absolute values of electrical units by the National Bureau of Standards and the re-evaluation of some of the fundamental constants by Dumond and Cohen,* with the co-operation of R. T. Birge.

Approximate values of some of these constants are given also on page viii.

One liter (1000 ml)	1000.028 cm^3
Standard acceleration of gravity	980.665 cm sec^{-2}
Standard atmosphere	1.013246×10^6 dynes cm^{-2}
Volume of ideal gas at 0° C, 1 standard atmosphere	22.4140 liters $mole^{-1}$ 22,414.6 cm^3 $mole^{-1}$
Ice point (0° C)	273.16° K
One calorie (defined)	4.1840 absolute joules
Gas constant per mole	8.3144×10^7 ergs $degree^{-1}$ $mole^{-1}$ 1.98718 cal $degree^{-1}$ $mole^{-1}$ 0.082,054 liter-atm $degree^{-1}$ $mole^{-1}$
Faraday constant	96496 abs. coulomb gram equivalent^{-1}
Avogadro number	6.0235×10^{23} $mole^{-1}$
Electronic charge	1.6020×10^{-20} absolute emu 1.6020×10^{-19} absolute coulomb 4.8024×10^{-10} absolute esu
Mass of electron	9.1055×10^{-28} g
Rydberg constant for H^1	109677.58 cm^{-1}
Rydberg constant for He^4	109722.26 cm^{-1}
Rydberg constant for infinite mass	109737.30 cm^{-1}
Planck's constant	6.6234×10^{-27} erg second
One absolute volt-electron	1.6020×10^{-12} erg $molecule^{-1}$ 23,063 cal $mole^{-1}$
Boltzmann constant (gas constant per molecule)	1.3803×10^{-16} erg $degree^{-1}$ $molecule^{-1}$
One kilocalorie $mole^{-1}$	6.9461×10^{-14} erg $molecule^{-1}$ = 0.043359 electron volt = 349.83 cm^{-1} (wave numbers) = 1.0487×10^{13} sec^{-1} (frequency)
Velocity of light in vacuum	2.99776×10^{10} cm sec^{-1}
1 international joule	1.000165 absolute joule
1 international volt	1.000330 absolute volt
1 international ohm	1.000495 absolute ohm
1 international ampere	0.999835 absolute ampere
Mass of proton	1.67229×10^{-24} g
Mass of neutron	1.67453×10^{-24} g

* Dumond and Cohen, *Rev. Mod. Phys.*, **20**, 82 (1948).

INTERNATIONAL ATOMIC WEIGHTS

1947

Published by the *Journal of the American Chemical Society*

	Symbol	*Atomic Number*	*Atomic Weight*		*Symbol*	*Atomic Number*	*Atomic Weight*
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.54	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.066
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

AUTHOR INDEX

Abramson, 541
Adair, 535
Adams, 239
Adkins, 386
Alberty, 543
Albright, 205
Alyea, 493
Anderson, 530, 638
Andrews, 666
Arrhenius, 250, 375, 517
Aston, 147
Averill, 662

Balmer, 571
Barr, 187
Baxter, 10, 662
Beattie, 475, 673
Beer, 79
Bell, 198
Bender, 583
Berkeley, 243
Bernet, 642
Berthelot, 19, 157, 254
Berthollet, 254
Bethe, 666
Bichowsky, 138, 181
Bingham, 190
Birge, 22, 635
Bjerrum, 493
Blasdale, 338
Blue, 147
Bodenstein, 387
Bohr, 570, 689
Boltzmann, 566
Bonhoeffer, 590, 613
Born, 589
Bowden, 338
Boyd, 554
Boyle, 5
Bradshaw, 401
Bragg, 47
Braun, 583
Bray, 387, 510
Bredig, 525
Bridgman, 582, 673
Briggs, 290, 338, 341
Britton, 552
Brockway, 85
Brode, 95
Brönsted, 493, 513
Brunauer, 550
Burton, 613
Butler, 121

Cady, 423, 533
Cailletet, 181
Campbell, 316, 338
Carothers, 526
Carnot, 676
Cassidy, 552
Chadwick, 641
Chalmers, 644
Charles, 6, 671
Chien, 583
Cholnoky, 552
Choppin, 367
Clapeyron, 174
Clark, 65, 85
Claude, 167
Clausius, 88, 177
Clusius, 635
Cohen, 699
Cohn, 527
Compton, 581, 657
Cope, 380
Cottrell, 561
Crawford, 219
Creighton, 427, 476
Crist, 264
Curie, 623, 644
Curtiss, 572

Dakin, 482
Dalton, 196, 204
Davey, 65
Davidson, 516, 666
Davies, 693
Davisson, 589

De Broglie, 589
Debye, 62, 88, 511, 512, 517, 518, 680
Deming, 338
Dempster, 633, 646
Derr, 434
Dickel, 635
Dirac, 589
Dole, 427, 463, 476, 519
Donnan, 556
Dufford, 608
Duggar, 611, 613
Duhring, 180
Dulong, 119
Dumond, 699

Ebert, 138
Edwards, 196
Ehlers, 491, 683
Einsporn, 577
Einstein, 102, 531, 533, 597, 655, 679
Ellis, 131
Emmett, 550
Essex, 302
Estes, 85
Evans, 65, 608
Ewell, 211
Ewing, 82, 482
Eyring, 189, 376, 389, 679, 690, 694

Fajans, 630
Falkenhagen, 518
Faraday, 407
Fenske, 386, 583
Fenwick, 462
Fermi, 643, 657
Ferry, 528
Findlay, 316, 338
Fisher, 92
Fletcher, 532
Flory, 526
Forbes, 602
Forsythe, 148
Foster, 380
Franck, 587
Frazer, 552
Freundlich, 540, 548, 561
Friedman, 58
Frolich, 386
Froslie, 586
Fuoss, 516, 518

Gamow, 666
Gay-Lussac, 6, 111, 671
Geiger, 625
Germann, 181
Germer, 589
Getman, v, 688
Giauque, 147, 148
Gibbs, 149, 316, 439, 547
Gibson, 147, 308
Gilkey, 181
Gilliland, 222
Gilman, 35, 40, 95, 488
Glasstone, 29, 95, 121, 162, 189, 190, 251, 295, 376, 389, 427, 476, 516, 519, 569, 590, 666, 678, 694
Glockler, 583, 635
Goodman, 662
Graham, 523, 527
Grant, 608
Greiff, 636
Griffing, 81
Groening, 423
Grotthus, 596
Guggenheim, 471
Guldberg, 254
Guntelberg, 681

Haber, 385
Hahn, 656
Hall, 493
Hammer, 490
Hammett, 519
Harkins, 547, 555, 641
Harned, 219, 427, 474, 476, 490, 491, 516, 519, 683, 688
Harteck, 590, 613
Hartley, 243
Hasche, 353
Hatschek, 190
Heisenberg, 581, 589
Helmholtz, 439
Henry, 202
Herb, 642
Hertz, 635
Herzberg, 590
Hess, 125
Heuse, 229
Heydweiller, 490
Hibben, 583
Higgins, 613

Hildebrand, 222, 251
Hill, 338, 341
Hinshelwood, 389
Hirschfelder, 92, 166, 380, 588
Hittorf, 409
Hoag, 666
Hofmeister, 560
Hogness, 367
Holt, 666
Horsley, 210
Hougen, 19, 133, 138, 162, 277, 288, 295, 693
Hubbard, 341
Hückel, 511, 512, 517, 680
Huffman, 131, 133, 138, 275, 286, 295
Hulburt, 588
Hull, 62, 328

Jackson, 62
James, 610, 613
Jenkins, 22
Johnson, 35, 40, 488
Johnston, 208, 347, 365, 693
Joliot, 644
Jones, 401
Joule, 111

Kamm, 82
Kassel, 390
Katzoff, 7
Kelley, 295
Kennard, 590
Kerst, 642
Ketelle, 554
Keyes, 169
Kharasch, 134
Kilpatrick, 138
King, 635
Kirchhoff, 565
Kistiakowsky, 133, 367
Knight, 181
Knipping, 46
Koehler, 427, 476
Kohlrausch, 490
Kolthoff, 308, 425, 502
Korff, 666
Kornfeld, 610
Kossel, 36
Kraemer, 561
Kraus, 418, 427, 516
Kruyt, 540

Laidler, 189, 376, 389, 694
Lambert, 78
La Mer, 513, 688
Lange, 16
Langmuir, 36, 551, 555
Lapp, 666
Lassettre, 38
Latimer, 147, 447, 476
Laue, 46
Lawrence, 642
Le Chatelier, 157
Leclanché, 475
Leermakers, 367
Leighton, 600, 602, 606, 613
Lewis, 36, 40, 120, 121, 138, 147, 149, 162, 217, 219, 276, 277, 469, 495, 507, 637, 685
Livingston, 387
Loeb, 29
Long, 547
Longsworth, 415
Lorentz, 69
Lorenz, 69
Lowry, 493
Luder, 495
Lundgren, 538
Lyman, 572

MacDougall, 162, 295
MacInnes, 414, 415, 427, 474, 475, 476, 484, 516, 519
Manning, 611
Mark, 534, 561
Marton, 530
Mathews, 76, 138, 215, 600
Mathias, 181
Maxwell, 368, 678
May, 308
McBain, 547, 552
McLeod, 84
McCormick, 583
Meads, 148
Mellon, 81
Migridichian, 290
Millard, 413
Miller, 112
Millikan, 532, 620
Moelwyn-Hughes, 40, 360

Montgomery, 616
Morse, 588
Morton, 215
Moseley, 621
Mosotti, 88
Murrell, 112
Müller, 425, 612, 625

Nagasako, 367
Nernst, 147, 387
Ness, 482
Newitt, 29
Newschwander, 482
Nier, 633
Nollet, 239
Noyes, 512, 600, 606, 613
Nutting, 547

Ohm, 396
Onsanger, 517, 518
Owen, 85, 427, 474, 476, 482, 516, 519, 688

Parkinson, 642
Parks, 131, 133, 138, 147, 275, 287, 295
Paschen, 572
Pasteur, 75
Patrick, 353, 551, 552
Pauli, 576
Pauling, 35, 38, 40, 65, 85, 95, 590
Pease, 389
Pederson, 533, 538
Pennington, 63
Perrin, 532
Peters, 454
Petit, 119
Pfeffer, 241
Pittsburgh staff, 590
Pitzer, 138, 275, 295, 691, 693
Planck, 565
Poiseuille, 187
Pollard, 666
Purdon, 338

Quayle, 85
Quiggle, 583

Rackett, 138
Radley, 608
Raman, 582, 583
Ramsay, 185, 196
Randall, 121, 138, 147, 162, 219, 277, 507, 685, 688
Rank, 583
Raoult, 202, 228
Rayleigh, 568
Reed, 350, 360
Reimers, 338
Reinmuth, 65
Remick, 488
Reuss, 541
Rice, 40, 666
Richards, 146
Richardson, 131
Richtmeyer, 590
Rideal, 190
Roberts, 462
Robertson, 688
Robinson, 222, 229
Rodebush, 38
Roebuck, 112
Roentgen, 620
Rollefson, 613, 616
Roseman, 7
Rosenblum, 502
Roseveare, 196, 350
Rossini, 131, 133, 138, 288, 294, 693
Rutherford, 638, 641

Sameshima, 277
Sänger, 89
Sargent, 469
Scatchard, 688
Scherrer, 62
Schrödinger, 589
Schumacher, 389
Schumb, 454
Seaborg, 646
Segre, 646
Seitz, 65
Selwood, 95
Semenoff, 388
Shadduck, 641
Shedlovsky, 484
Sherman, 40
Sherwood, 360
Shields, 185
Shoenheimer, 663
Shuler, 58
Sidgwick, 40, 91

Siedentopf, 528
Sinclair, 229
Slater, 338
Smith, 332, 367, 552
Smoluchowski, 540
Smyth, 91, 95
Soddy, 630
Sorensen, 535
Starkweather, 10
Staudinger, 562
Stauffer, 611
Steacie, 389
Stefan, 566
Steiner, 121, 162, 295
Steno, 44
St. Gilles, 254
Stillwell, 65
Stockhardt, 328
Stokes, 531, 608
Strassman, 656
Stosick, 86
Style, 613
Sugden, 84
Svedberg, 533, 537, 538, 561
Sweetzer, 454
Swietoslawski, 251
Szillard, 644, 657

Tartar, 482
Taylor, 138, 264, 474, 561, 569, 590, 635, 666
Teller, 550
Theriault, 350
Thilorier, 167
Thomson, 111, 630
Tiselius, 542, 552, 553
Tonberg, 208
Travis, 524
Trouton, 182
Tyndall, 528

Urey, 636, 637, 639

Van der Waals, 15, 204, 672
Vanselow, 688
Van't Hoff, 241
Van Vleck, 40
Verhoek, 276
Vold, 530
Volta, 431
Vosburgh, 434

Waage, 254
Walter, 690
Washburn, 229, 413, 637
Waters, 434
Watson, 19, 133, 138, 162, 181, 277, 288, 295, 693
Wegand, 583
Weiser, 561
Welch, 211
Wenner, 138, 286, 295, 691, 693
Werner, 138
Weston, 433
Wien, 518, 568
Wigner, 657
Williams, 76, 138, 205, 215, 533, 538, 600
Williamson, 292
Willows, 190
Wilson, 590, 625, 690, 693
Winans, 586
Winninghoff, 510
Wolff, 434
Wolthius, 85
Wood, 547
Woolsey, 19
Wright, 198
Wyckoff, 65

Zachariasen, 65
Zawidski, 199
Zcheile, 82
Zechmeister, 552
Zsigmondy, 528
Zuffanti, 495

SUBJECT INDEX

A, angstrom, 61
A, work content, 149
Absorption, and chemical structure, 81
  coefficient, 79
  of light, 565
  spectrum, 81
Acids, ionization constants, 487
Actinometer, 602
Activated complex, Eyring theory, 376
Activation energies, calculation, 694
Activation energy, 373, 380
Activities, 276, 469
  from electromotive force, 682
  from freezing points, 686
  of electrolytes and ions, 469
  of mercury in thallium amalgams, 686
  of solvent from activities of solute, 684
Activity coefficient, 470, 473, 474
  of hydrochloric acid, 684
Additive property, 67
Adiabatic expansion of gas, 112
Adsorption, by silica gel, 549
Age of the earth, 662
Alpha rays, 623, 639
Amorphous solids, 42
Ampere, 396, 397, 699
Angstrom, 61
Anisotropic crystal, 42
Annihilation of matter, 655
Anode, 405, 407, 444
Aqua, 124
Arrhenius equation, 377
Arrhenius theory, 250, 517
Asymmetric carbon atom, 73
Atomic energy commission, 660
Atomic forces, 33
Atomic mass, 634
Atomic models, 92
Atomic number, 620, 621, 622
Atomic power, 658
Atomic refractions, 71
Atomic structure, 617
Atomic weight, 634, 640
  table, 700
Avogadro constant, 8, 532, 626
Avogadro law, 8
Azeotropic solution, 211

Bacteriophage, picture, 530
Band spectroscopy, 584
Barostat, 233
Battery, 432
Beattie–Bridgman equation, 673
Beer's law, 79
Berthelot's equation, 19
Beta rays, 623
Bimolecular reactions, 344
Binary mixtures, 209, 210
Biological applications of photochemistry, 610
Bohr's theory, 570, 689
Bond radii, 92
Boiling point, constants, 231, 237
  elevation, 229, 244
  determinations, 232
Boiling points, table, 14
Boyle's law, 671
Bragg X-ray analysis, 47
Brownian motion, 530
Buffer solutions, 501, 502
Bunsen coefficient, 203

C, heat capacity, 108
Cadmium cell, 433
Calculus, 696
Calomel electrode, 435
Calorie, 101, 124, 699
Calorimetric measurements, 124
Carnot cycle, 676
Catalysis, 382, 383
Cathode, 405, 407
Cells, classification, 441
  reversible, 438
  with junction potential, 442
  without transference, 442, 471
Chain reactions, 387, 389, 603
Characteristic solutions, 589
Chemical and electric energy, 438

Chemical equilibria, 254
and electromotive force, 450
and temperature, 280
Chemical kinetics, 342
Chemiluminescence, 608
Chlorophyl, 611
Clapeyron equation, 174
Claude process, 167
Clausius–Clapeyron equation, 177, 230
Cloud chamber, 625
Collision frequency, 370
Collisions, molecules and protons, 593
Colloidal electrolytes, 556
Colloid mill, 524
Colloids, 523
by arc method, 525
definition, 523
dispersion methods, 524
electrical behavior, 539
kinetic behavior, 530
particle weights, 539
precipitation by electrolytes, 545
preparation, 524
purification, 527
optical behavior, 528
stability, 544
Competing reactions, 354
Complex ions, 515
Complex reactions, 354
mathematical analysis, 357
Compton effect, 581
Concentrated solutions, 514
Concentration cells, 454
electromotive force, 683
Conductance, at different temperatures, 405
equivalent, 400
measurements, 398
molar, 400
of electrolytes, 403
of fused salts, 420
of gases, 617
on nonaqueous solutions, 418
of potassium chloride, 401. 402
specific, 400
theories, 516
Conductimetric titrations, 420
Consecutive reactions, 354, 358
Conservation, of energy, 102
of mass, 102
Constitutive property, 67
Conversion electrons, 645
Cooling curves, 321
Coordinate covalent bond, 37
Copper–zinc cell, 432
thermodynamics, 153
Cosmic rays, 644, 661
Coulomb, 396
Critical constants, table, 14
Critical potentials, 576
Critical pressure, 12
Critical temperature, 12, 14
Critical volume, 12
Crystal forms, 42
Crystal lattice of sodium chloride, 52, 54
Crystals, binding forces, 58
properties, 59
Crystal structure, 47, 59
Cubic lattices, 49
Cyclotron, 642

Dalton's law, 196
Debye–Hückel theory, 511, 517, 680
Decomposition, of hydrogen peroxide, 387
of nitrogen pentoxide, 348, 366
Decomposition voltage, 422
Degrees of freedom, 118, 317
Δ, delta, 102, 696
Densities, abnormal, 23
of nitrogen tetroxide, 259
Deuterium, 637, 639, 664
Deuteron, 639
Dialysis, 527
Dielectric constant, 87
Differential absorption, 552
Differential heat of solution, 220
Diffusion, 531
rate, specific, 688
Dipole–dipole attraction, 39
Dipole moments, 87
table, 90
Disintegration of the radioelements, 627
Disperse system, 523
Dispersing medium, 523
Dispersoids, 523
Dissociation, energy, 587
of gases, 258
of hydrogen iodide, 264
of solutes, 248

Dissociation, pressures of $CaCO_3$, 289
Distance between 111 planes, 673
Distillation, fractional, 212
  of binary systems, 211
Distribution of bromine, 293
Donnan membrane equilibrium, 556
Dropping mercury electrode, 425
Duhring's rule, 181
Dulong and Petit rule, 119
Dyne, 99

E, internal energy, 102
E, voltage, electromotive force, 438
Einstein, displacement formula, 532
  equation of mass and energy, 102, 597
  photochemical law, 655
Electrical resistances, typical, 398
Electrical units, 396
Electric conductance, 395
  historical introduction, 395, 397
Electrochemical conventions, 442
Electrode, hydrogen, 457
Electrode potentials, table, 447
Electrode reactions, 441
Electrodes, for hydrogen ions, 460
  reference, 434
  types, 441
Electrokinetic potential, 540
Electrolysis, 405
  reactions, 407
Electrolytes, concentration ranges, 515
Electrolytic dissociation theory, 250
Electrolytic reduction and oxidation, 426
Electromagnetic unit, 396
Electromotive force, 431
  and chemical equilibria, 450
Electron, 618, 639
  charge, 620
Electron microscope, 529
Electron pair, 35
Electron theory of valence, 35
Electrons, diffraction, 85
  energies, 693
  ratio of mass to charge, 619
  velocity, 619
Electroosmosis, 543
Electrophoresis, 541, 542
Electrostatic attractions, 38
Electrostatic generator, 642
Electrostatic unit, 396
Electrotitration, 464, 467
Elliptical orbit, 689
Elution, 554
Emission of light, 565, 567
Emulsifying agent, 558
Emulsions, 558
Endothermic reactions, 124
Energies, electronic, 595
  rotational, 595
  vibrational, 595
Energy, forms, 99
  intensity and capacity factors, 100
  levels in hydrogen atom, 573
  map for addition of bromine, 695
Enthalpy, 107
Entropies, table, 149
Entropy, 143
  calculations, 145
  of activation, 380
Enzymes, 387
Equations of state, 18
Equilibria, between solids and gases, 288
  in immiscible solvents, 292
  in solutions, 267
Equilibrium, constants, 255
    from enthalpy and entropy, 286
    in gases, 260
    of nitric oxide, 281
  determination, 257
  pressures of NH_4HS, 290
Equipartition of energy, 569
Equivalent conductance, 400
Erg, 3, 99
Eutectic temperature, 320
Exothermic reactions, 124
Expansion of gas, 105, 413
Extinction coefficient, 79
Eyring's equation, 679
  theory of reaction rates, 376, 679, 694

F, faraday, 438
F, free energy, 149
Faraday's law, 407
First law of thermodynamics, 101
First-order reaction, 345, 367
Fischer–Tropsch synthesis, 386
Fission, 656
  products, 659
Fluidity, 189
Fluorescence, 594, 608

Fractional distillation, 212
Fractionating column, 213
Free energy, 149
  and chemical reaction, 153, 268
  influence, of pressure, 152
    of temperature, 283
  of dilution, 244
  of formation, table, 275
  tables, 273
Free radicals, 389
Freezing point, constant, 236
  determination, 238
  lowering, 233, 244, 249
Frequency, factor, 376
  of collisions, 370
  of light, 77
  of radiation, 598
Fugacities, 276
Fundamental units, 3

Galvanic cells, 431
γ, gamma, 470
Gamma rays, 623
Gas constant, 7
Gas density, 9
  and dissociation, 258
Gaseous state, 5
Gases, ideal, 5
  real, 10
Gas law and partial differentiation. 671
Geiger–Müller counter, 625
Gels, 559
Gibbs equation, 547
Gibbs–Helmholtz equation, 161, 439, 440
Glass electrode, 462
Greek alphabet, 697

H, enthalpy, 107
Haber process for ammonia, 385
Half-life, 347
Heat, 99
  absorption, 106
  capacity, 99, 108
    and temperature, 134
    of gases, 115
      influence of temperature on, 117
      table, 116
    of silver, 148
    of solids, 118
Heat, content (*see* enthalpy), 107
  of activation, 373, 374, 376
  of combustion, 131
    table, 132
  of dissociation of bonds, 134
  of formation, 127
    table, 129
  of reaction and temperature, 136
  of solution, 219
    molal, 219
    partial molal, 220
    sodium chloride, 222
  of vaporization, 182
Heavy water, 637
Henry's law, 202
Heterogeneous systems, 304
Heteropolar bonds, 35
Homopolar bonds, 35
Hougen and Watson chart, 20
Hydrogenation catalysts, 385
Hydrogen bond, 200
Hydrogen electrode, 435, 457
Hydrogen-ion activities, 459
Hydrogen spectrum, 572
Hydrolysis, 496
  constant, 498
  degree, 497
  of ethyl acetate, 352
Hypothesis, 4

Ice, 309
Immiscible liquids, 216
Indicators, 502
Induced-dipole attraction, 40
Industrial colloids, 561
Infrared-absorption spectrum, 585, 595
Infrared conversion graph, 600
Integral heats of solution, 221
Interface, molecular orientation at, 554
Interfacial tension, 546
Interionic attraction, 509, 511
Internal energy of gases, 110
International electrical units, 396, 699
Ionic conductances, 416
  at infinite dilution, 417
Ionic equilibria, 483
Ionic mobilities, 414
Ionic strength, 507
  and strong electrolytes, 508
Ion–ion attraction, 39

Ionization, chambers, 625
constant of acetic acid, 485
of acids, 489
of bases, 487
of water, 490
of weak electrolytes, 483
potential, 578
Isoelectric point, 545
Isomeric transition, 645
Isomorphous crystal, 43
Isothermals, 12
Isotopes, 630, 683
concentration, 635
of cadmium, 633, 646
of lead, 632
occurrence, 633
table, 647–654
thermal diffusion, 635
uses, 661
Isotropic crystal, 42

Joule, 101
Joule–Thomson effect, 167, 675
Junction potentials, 468

K, equilibrium constant, 225
k, specific rate constant, 346
K-electron capture, 644
Kilocalorie, 124
Kinetic energy, 27
Kinetic equation, 27
and heat capacity, 115
Kinetics, chemical, 342
photochemical, 602
Kinetic theory of gases, 25, 367
Kohlrausch's law, 416

Langmuir theory of adsorption, 550
Lattice units in crystals, 55
Laue X-ray pattern, 46
Lead storage battery, 475
Le Chatelier's theorem, 157, 177
Light, absorption, 75
transmission, 80
Limiting densities, 22
Linde process, 167
Liquefaction of gases, 166
Liquid junction, 411, 468
Liquid state, 166
Logarithms, back cover
Luminescence, 608
Lyman series, 572
Lyophobic colloids, 524
Lyophylic colloids, 524, 544
Lyotropic series, 560

m, molal, 195
M, molar, 195
Mass law, 254
Mass numbers, 634
Mass spectrometer, 631
Mathematical formulas, 696
Maximum boiling points, 208
Maximum work, isothermal expansion, 105
Maxwell–Boltzmann equation, 692
Maxwell distribution law, 368, 678
Mean free path, 372
Meson, 639
Migration of ions, 409
Miller indices, 45
Millimicron, 76
Minimum boiling points, 208
Molal solution, 195
Molar solution, 195
Molar conductance, 400
Molar refraction, 69
Molecular collisions in gases, 370
Molecular diameters, 371
Molecular forces, 33
Molecular structure, and ionization, 488
and physical properties, 67
methods, 95
Molecular weights, 9, 21
Mole fraction, 195
Monochromator, 600
Morse curve, 589
μ, mu, 523
Mutations, 612

Neutron, 637, 638, 639
Nonpolar compounds, 35
Normal solution, 194
Nuclear chain reaction, 657
Nuclear fission, 656
Nuclear isomers, 645
Nuclear reactions, 355, 644, 645, 646
Nuclear structure, 617
Nuclear units, 638, 639
Nuclei, composition, 640
Number of molecules striking a surface, 370

Ohm, 396
Optical activity, 73
Order of reaction, determination, 362
Ortho-hydrogen, 590
Osmosis, 239
Osmotic pressure, 239, 241, 242, 244
Overvoltage, 426
Oxidation, 406
  by removal of electrons, 406, 426
  electrode potentials, 443, 446
  reactions, 443
Oxide electrode, 462

Packing fraction, 655
Parachor, 83
Para-hydrogen, 590
Partial differentiation, 671, 675
Partial miscibility, 328
Partial molal quantities, 217
Partial molal volumes, 218
Partial pressure, Dalton's law, 196
  of solutions, 199, 201
Particle weight, 534
Partition function, 692
Paschen series, 572
Pauli's exclusion principle, 576
Percentage by weight, 195
Periodic classification of the elements, 665
Periodic table, 665
*p*H, 459, 463, 464
Phase, 304
Phase diagram, 304
  bismuth–cadmium, 322
  cobalt–chromium, 329
  concentration and temperature, 319
  copper sulfate and water, 314
  for partially miscible liquids, 329
  for sulfur, 311
  gold–aluminum, 332
  molybdenum–cobalt, 330
  platinum–gold, 327
  sulfuric acid and water, 325
  triangular, ~~323~~ 332
  uses, 331
  water, 308
  with chemical interaction, 323
  zinc–magnesium, 324
Phase rule, 316, 318
Phosphate glasses, 338
Photocells, 77
Photochemical kinetics, 602
Photochemical reactions, 606
Photochemistry, 593
  experimental procedure, 600
  laws, 596
Photoelectric cell, 580
Photoelectric effect, 579
Photography, 609
Photon, 594
Photosensitization, 605
Photosynthesis, 611
Physical-chemical constants, table, 699
Physical chemistry, survey, 1
Physical properties and molecular structure, 67
Pile, 657
Planck's constant, 569
Planck's formula, 569
Poise, 187
Polar compounds, 35
Polarimeter, 72
Polarization, electrode, 426
  molar, 87
Polarized light, rotation, 71
Polymerization, 526
Positron, 638, 639
Potentials, electrode standard, 447
  electrokinetic, 540
  zeta, 540
Potentiometer, 436
Potentiometric titrations, 463
  method of tangents, 467
Pressure–volume relations of gases, 11
Protective colloids, 546
Proton, 639
  theory of acids, 493

q, heat, 102
Quantum mechanics, 589
Quantum numbers, 574, 576
Quantum theory, 565, 568
Quantum yields, 604, 606
Quinhydrone electrode, 460

Radiation intensity, 567
Radiation laws, 566
Radiations, energy, 599
Radioactive carbon, 663
Radioactive elements, production, 641, 644
Radioactive equilibrium, 628

Radioactivity, biological effects, 660
geological applications, 662
measurement, 624
Radioelements, and periodic table, 630
disintegration, 629
Radio indicators, 663
Radium, discovery, 623
Radon, 624
Raman effect, 582
Raman spectrum of carbon tetrachloride, 584
Raoult's law, 202, 227
Rate equation, 679
Rayleigh law, 568
Reaction mechanisms, 344
Reaction rate constants, calculation, 345, 350, 353
Reaction rates, measurements, 342
temperature, 365
prediction, 377
Reduction by addition of electrons, 406, 426, 442
Reduction–oxidation indicator, 504
Refractions, table of molar, 70
Refractive index, 67, 68
calculation, 674
Relativity theory, 620, 655
Repression of ionization, 488
Resonance, 38, 94
potentials, 578
Reverse reactions, 354
Reversible cells, 438
Reversible processes, 103
Rotational energies, 693
Rotation, molar, 74
specific, 73
Rydberg constant, 571, 573

S, entropy, 143
Salt bridge, 434
Salting-out effect, 204, 294
Saturated solution, 305
Scientific method, 4
Second law of thermodynamics, 142
Second-order reactions, 350
Sedimentation equilibrium, 535
Sedimentation velocity, 538
Semipermeable membrane, 239, 240
Silica gel, 550, 559
Solids, properties, 42
Solid solutions, 326
Solubility, 305
n-butanol and water, 305
of gases, 203
of solids, 307
product, 504, 505
influence of salts, 511
temperature, 306
Solution, binary, 194
molal, 195
molar, 194
normal, 194
Solutions, 194
composition, 194
ideal, 197
nonideal, 197
of gases, 196
in liquids, 202
of nonvolatile solutes, 227
Solvates, 514
Space model for two salts and water, 337
Specific conductance, 400
Specific reaction rate constant, 346
Specific refraction, 69
Spectra, types, 594
Spectral lines and critical potentials, 579
Spectrophotometer, 77
Spectroscopy, 570
Spontaneous change, 155
criteria for, 157
Standard cells, 433
Standard electrode potentials, 447
Stark effect, 574
Statistical thermodynamics, 690
Staudinger equation, 534
Steam distillation, 217
Stefan–Boltzmann law, 566
Steno's law, 44
Stokes's law, 531
Streaming potential, 543
Strength of acids, 494
Strong electrolytes, classification, 506
Supersaturated solutions, 308
Surface tension, 184, 186
Symbols, table, 698
Syneresis, 560
Synthesis of methanol, 386

T, absolute temperature, 5
t, temperature, centigrade, 5
Temperature, and equilibrium constants, 280

Temperature, and heat capacity, 134
and heat of reaction, 136
and reaction rate, 379
Theoretical plates, 213, 215
Theory, 4
Thermal analysis, 321
Thermochemical constants, 133
Thermochemistry, laws, 124, 125
Thermodynamic calculations, 157
Thermodynamics, 99
first law, 101
second law, 142
third law, 146
Thermopile, 600
Third-order reactions, 353
Three-component systems, 332
Tie line, 333
Tracer elements, 664
Transference numbers, 409
by change in concentration, 411
by electromotive force, 474
by moving boundary, 414
Transition temperature, 311
Translational energies, 693
Transmutation, 641, 664
Triangular coordinates, 333
Triangular diagram, 335
Triangular prism, 335
Trigonometry, 697
Triple point, 310
Trouton's relation, 182
Two-component systems, 318
Tyndall effect, 528

Ultracentrifuge, 536
Ultrafiltration, 527
Ultramicroscope, 528
Ultraviolet light, 595, 599
Unimolecular films, 554
Unimolecular reaction, 344
Units, fundamental, 3
Uranyl oxalate actinometer, 602

Valence, 35
Van der Waals, constants, 16, 672
equation, 15, 204
Vapor composition of binary systems, 206
Vaporization, entropy, 183
of liquids, 103
Vapor pressure, curves, 170
Vapor pressure, gas-saturation method, 173
lowering, 229
measurement, 172
of acetone–ether solutions, 278
of liquids, 169
table, 171
Vapor relationships, empirical, 181
Velocity, of light, 77, 598, 699
of molecules, 28
Velocity constant, 346
Vibrational energies, 693
Victor Meyer method, 10
Virial equation, 19
Viscometers, 188
Viscosity, 533
and temperature, 188
of colloids, 533
of liquids, 188
Vitamin D, 612
Volt, 396
Voltage and oxidizing and reducing ions, 454
Voltage measurement of cells, 436
Voltmeter–potentiometer, 435

w, work, 102
Water, 309, 637
Watt, 396
Wave length, 598
Wave number, 571, 572
Weights, atomic, 634, 640
Weston cell, 433
Wheatstone bridge, 399
Wien's law, 568
Work, 99
Work content, 149
Work conversion from heat, 160

X-ray analysis of crystalline powders, 62
X rays, 46
applications, 63
wave length, 60
X-ray spectrometer, 48

Z, atomic number, 621
Zeeman effect, 574
Zero-order reactions, 353
Zero-point energy, 588
Zeta potential, 540

Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Natural Numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4